(1,3,5-trioxanyl)succinate: yield, 1.74 g (26.6%); bp 140–145° (1 mm); $n^{18}D$ 1.4422; nmr, multiplet centered at 4.9 (5 H, $-OCH_2OCHOCH_2-$), two quartets at 5.8 and 5.9 (4 H, $-OCH_2-CH_3$, J = 7 cps), multiplets centered at 6.8 (1 H, $-CHCOOC_2H_5$) and at 7.22 (2 H, $-CH_2COOC_2H_5$), and a triplet at 8.76 (6 H, $-CH_2CH_3$, J = 7 cps).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.37; H, 6.92. Found: C, 50.67; H, 7.02.

The 2,4-dinitrophenylhydrazones of diethyl formyl succinate and of formaldehyde were obtained by the usual procedure. The same solvent mixture eluted bi-1,3,5-trioxan (1 g). Acetone–alcohol mixtures eluted polar oils.

1,3,5-Trioxan, Diethyl Maleate, and Acetophenone with Ultraviolet Light (at 65–70°).—The reaction was carried out with diethyl maleate (4.3 g), 1,3,5-trioxan (150 g), and acetophenone (8 ml). The usual work-up led to 5.4 g of unchanged acetophenone, 5.5 g (84%) of diethyl (1,3,5-trioxanyl)succinate, and polar oils (5.2 g).

Anal. Found: C, 52.68; H, 7.55.

1,3,5-Trioxan and Diethyl Maleate with Ultraviolet Light (at 65–70°).—A mixture of diethyl maleate (1 g) and 1,3,5-trioxan (150 g) was irradiated (quartz filter) for 1 hr. Diethyl maleate (3.3 g) was then added in three equal portions at 1-hr intervals and the mixture was irradiated for another 4 hr. The usual work-up led to diethyl (1,3,5-trioxanyl)succinate (1.5 g, 23%). Under similar reaction conditions, but using a Pyrex filter, diethyl (1,3,5-trioxanyl)succinate could not be detected.

Registry No.—2-Decyl-1,3-dioxolan, 6316-24-1; 4-decyl-1,3-dioxolan, 15138-46-2; 2,2′-bi-1,3-dioxolan, 6705-89-1; 2-octyl-1,3-dioxolan, 5432-30-4; 4-octyl-1,3-dioxolan, 15138-49-5; 2-heptyl-1,3-dioxolan, 4359-57-3; 2-dodecyl-1,3-dioxolan, 15138-51-9; 4-dodecyl-1,3-dioxolan, 15138-52-0; methyl 11-(1,3-dioxolanyl-2)undecanoate, 3515-98-8; methyl 12-hydroxy-12-methyltridecanoate, 15138-54-2; 12-hydroxy-12-methyltridecanoic acid, 15138-55-3; methyl 5-(1,3-dioxolanyl-2)pentanoate, 15138-56-4; methyl 5-formylvalerate 2,4-dinitrophenylhydrazone, 15138-57-5; methyl 6-hydroxy-6-methylheptanoate, 15188-17-7; diethyl (1,3-dioxolanyl-2)succinate, 15188-18-8; diethyl formylsuccinate 2,4-dinitrophenylhydrazone, 15188-19-9; decyl-1,3,5-trioxan, 14596-81-7; bi-1,3,5-trioxan, 15188-21-3; octyl-1,3,5-trioxan, 14596-80-6; heptyl-1,3,5-trioxan, 14596-79-3; dodecyl-1,3,5-trioxan, 15188-24-6; methyl 11-(1,3,5-trioxanyl)undecanoate, 15188-25-7; methyl 5-(1,3,5-trioxanyl)pentanoate, 15188-26-8; diethyl (1,3,5-trioxanyl)succinate, 15188-27-9.

Acknowledgment.—Support of this work by a grant from the National Council for Research and Development is gratefully acknowledged. The authors wish to express their appreciation to Dr. M. S. Gibson for most valuable discussions and comments during the course of this work.

Compression Effects in 1,4-Di-*t*-butylnaphthalenes. Chemistry and Nuclear Magnetic Resonance Spectra[1]

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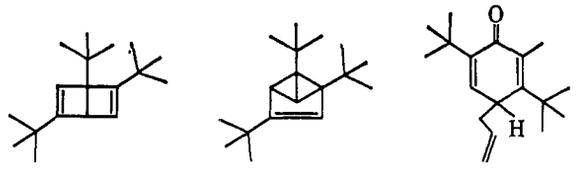
Received July 27, 1967

The syntheses of the 1,4-di-*t*-butylnaphthalenes **5**, **6**, **7**, **11**, **14**, and **15** are described. A compression effect of a *t*-butyl group in the acid-catalyzed rearrangement of endoxide **5** is detected. The effect is the addition of an external nucleophile to a benzcyclohexadienyl cation rather than the usual elimination of a proton to form a naphthalene. The air-sensitive naphthol **11** is examined for the possible presence of a ketone tautomer. The nmr spectra of the *peri* protons in the above compounds reveal a deshielding phenomenon attributed to a compression effect. An intramolecular nuclear Overhauser effect (NOE) is detected.

The effect of *t*-butyl crowding in benzenes has been examined in several ways. The stabilization of nonaromatic valence isomers, **1–3**, because of steric hin-



1 2 3

drance in the planar aromatic species is a striking result.[3] The change in the relative height of activation barriers in the steps of electrophilic aromatic substitution has been accomplished through a similar steric destabilization of the planar aromatic product.[4] An extension of the area of investigation to the potentially more crowded *peri*-*t*-butyl group in 1,4-di-*t*-butylnaphthalenes is described in this report.

Our synthetic entry to the naphthalenes (Chart I) is *via* the aprotic diazotization of 2,5-di-*t*-butylaniline **4** in the presence of furan to afford 5,8-di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (**5**) in 21% yield.[5]

The structure of adduct **5** is based on its further conversions (*vide infra*) and on its very symmetrical nmr spectrum. The *t*-butyl protons at δ 1.30 and the aromatic protons at 6.77 were narrow singlets while the benzylic pair at 5.95 and the vinyl protons at 6.87 were identically shaped narrow multiplets indicative of an AA′BB′ system. Hydrogenation of endoxide **5** affords saturated endoxide **6** (97%). Dehydration with ethanolic hydrogen chloride yields 1,4-di-*t*-butylnaphthalene **7** in 94% yield. The richly

(1) (a) Supported by the National Science Foundation, Grant GP 5160. (b) Parts of this research have been reported in preliminary form: Abstracts, Second Middle Atlantic Regional Meeting of the American Chemical Society, Feb 1967, p. 67; R. W. Franck and K. Yanagi, *Tetrahedron Letters*, 2905 (1966); R. W. Franck and K. Yanagi, *ibid.*, 1789 (1967).

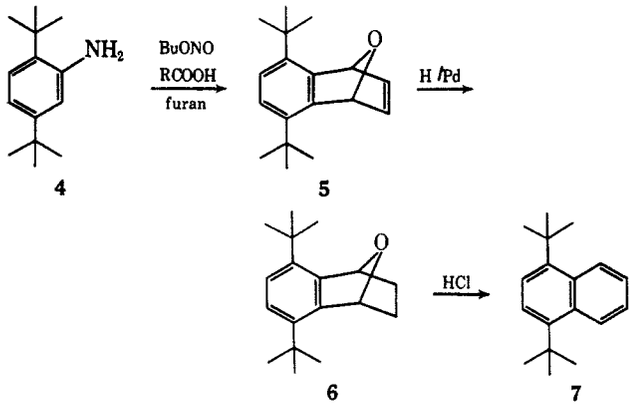
(2) On leave from Research Institute of Science and Industry, Kyushu University, Fukuoka, Japan.

(3) (a) E. van Tamelen and S. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962), (b) K. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965); (c) B. Miller, *ibid.*, **89**, 1685 (1967).

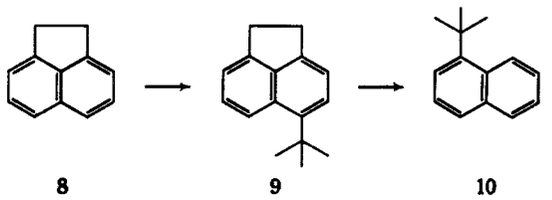
(4) (a) P. C. Myhre and M. Beug, *ibid.*, **88**, 1569 (1966); (b) E. Baciocchi, G. Illuminati, G. Sleiter, and F. Stegel, *ibid.*, **89**, 125 (1967).

(5) The detailed mechanism of this unusual reaction is the subject of a separate paper: K. Yanagi and R. W. Franck, manuscript submitted for publication.

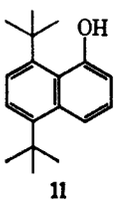
CHART I



detailed uv spectrum[6] (λ_{max}^{EtOH} 316 mμ (log ε 2.72), 298 (3.81), 286 (3.96), 276 (3.86), 267 s (3.65), 256 s (3.36), 221 (4.90), 214 s (4.73)) and the nmr (*vide infra*) are in accord with structure **7**, making it the first 1-*t*-butylnaphthalene derivative that is reasonably accessible.[7] The catalytic hydrogenation of **7** has revealed an unusual preference for reaction with the substituted ring.[7b] The release of *peri* strain in the transition state is assumed to be the driving force for this novel result. All direct routes *via t*-butylation of naphthalene have resulted in the formation of a 2,6–2,7 mixture.[7] The *t*-butylation of acenaphthylene **8** affords some 3-*t*-butyl product **9** which can be converted to 1-*t*-butylnaphthalene **10**[8] in 1% over-all yield. A yield of 2% of **10** has been obtained through a route using 1-tetralone and *t*-butyl Grignard reagent.[8]

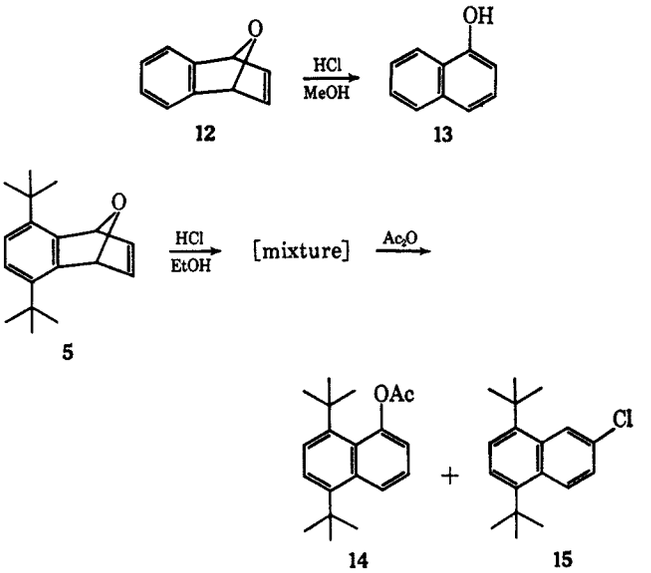


Proton-catalyzed rearrangement of endoxide **5** to naphthol **11** was attempted, with the hope of



paralleling the facile, quantitative conversion of unsubstituted endoxide **12** to α-naphthol **13**.[9] Conditions for the reaction were devised using ethanol saturated with anhydrous hydrogen chloride (Chart II).

CHART II



In work-up by chromatography, the eluted products were not homogeneous (as determined by gas chromatography), usually violet, and exhibited carbonyl bands in their ir spectra (*vide infra*). A modified work-up of the rearrangement products of endoxide **5** was used; following the removal of the ethanolic hydrogen chloride from the reaction mixture, acetic anhydride was introduced and was refluxed for 4 hr. Gas chromatographic analysis of the cooled acetic anhydride solution revealed two major components (72 and 16% of the total area) which could be separated by column chromatography on silica gel. The major product was identified as 1,4-di-*t*-butyl-5-naphthyl acetate **14**.

The minor product contained chlorine and was clearly shown (by nmr *vide infra*) to be 1,4-di-*t*-butyl-6-chloronaphthalene **15**. The appearance of this β-substituted product in the di-*t*-butyl series prompted our reexamination of the unsubstituted endoxide **12**. No 2-chloronaphthalene or any other impurity could be detected by the vpc analysis of the product α-naphthol. Of several "paper" rationales that can be devised for our result, the one given in Chart III was considered most likely. The initial step in the acid-catalyzed reaction is probably protonation of oxygen and ring opening to form the benzohydroxycyclohexadienyl cation A. In simple unsubstituted cases, proton elimination at C_1 results in aromatization. In the 1,4-dimethylendoxide **16**, aromatization of the cation B cannot occur; thus methyl migration and external solvent attack yield products **17** and **18**, respectively.[10] One could postulate that the di-*t*-butylbenzocyclohexadienyl cation C, when formed, is slow to aromatize because shortening of the 1,9 bond, and concomitant eclipsing of the hydroxyl and *t*-butyl groups raises the activation energy of the proton-elimination step. Thus, addition of external nucleophile can become competitive, generating dihydronaphthalene **19**. (Nucleophilic attack at C_4 seems unlikely because of the repulsions of the other *peri*-*t*-butyl group). Elimination of water from **19** would

(6) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Spectrum No. 201 as a model.

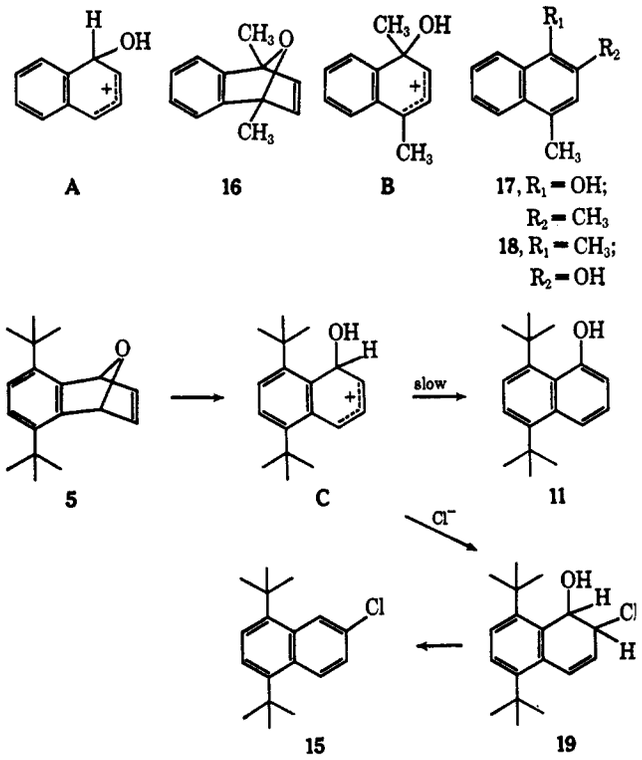
(7) (a) A. Schreisheim, "Friedel–Crafts and Related Reactions," Vol. II, part 1, G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, Chapter XVIII. (b) An independent, as yet unspecified, six-step synthesis of **7** has recently been reported: H. van Bekkum, T. J. Nieuwstad, J. van Barneveld, and B. M. Wepster, *Tetrahedron Letters*, 2269 (1967).

(8) E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).

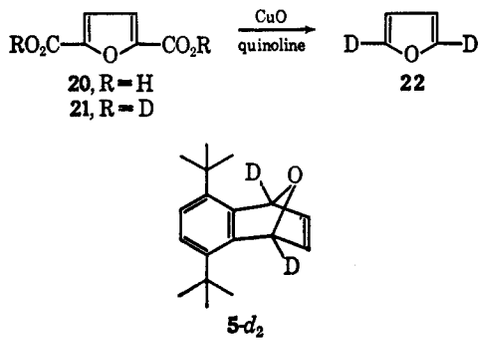
(9) G. Wittig and B. Pohmer, *Chem. Ber.*, **89**, 1349 (1955).

(10) (a) E. Wolthuis, B. Bossenbroek, G. De Wall, E. Geels, and A. Leegwater, *J. Org. Chem.*, **28**, 148 (1963); (b) M. Fetizon and N. T. Anh, *Bull. Soc. Chim. France*, 3209 (1965).

CHART III

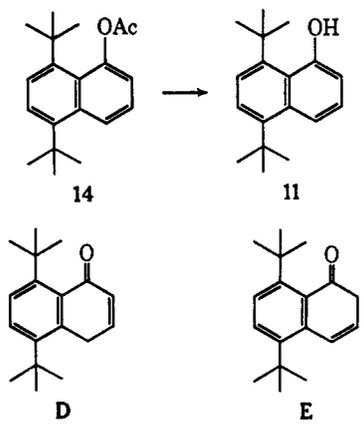


afford the observed chloro compound **15**. If the activation energy of the proton elimination from C is a factor in chloro compound formation, then rearrangement of **5**-d_2 *via* C-d_2 should result in an observable change in product ratio. The desired substrate, 15.3% d_0, 42.3% d_1, 35.0% d_2, 6.5% d_3, 0.9% d_4, was synthesized *via* the diazotization route using deuterated furan **22**. The furan was prepared by decarboxylation of furan-2,5-dicarboxylic acid-O-d_2 **21** with cupric oxide in hot quinoline. The integrated inten-

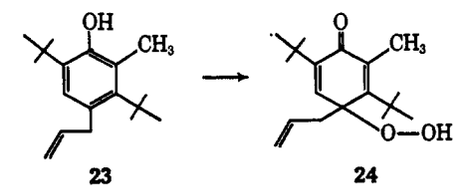


sity of the α protons was 45% of that of the β protons in the nmr of the product. Apparently the diacid in hot quinoline can act as a catalyst for the exchange of aromatic protons in the quinoline. The deuterated acid **21** was prepared by recrystallizing the protio acid **20** from dimethylformamide–heavy water. Work-up of the rearrangement products of the **5**-*d* species afforded naphthol acetate **14** in 56% yield and chloronaphthalene **15** in 29% yield. Corrections for protio intermediate which would rearrange in the original ratio must be made. The 15.3% d_0 species must be included, and the d_1 species which can ring-open in two ways must be considered. Using the secondary isotope effect determined for the solvolysis of benzyl tosylate k_H/k_D 1.12, one could calculate that the 42.3% d_1 would open to form 22.3% of intermediate C with deuterium at C_1 and 20.0% with hydrogen at C_1.[11] Then the corrected yields for product formation from **5**-*d* species are 49% of acetate **14** and 36% chloro compound **15**. Now, a partitioning isotope effect may be calculated. The ratios of acetate to chloro compound follow: k_H **14/15** = 4.50; k_D **14/15** = 1.36; or $k'H/D$ = 3.31. This observation is strong evidence for a compression effect on intermediate C forcing a diversion from the "normal" elimination pathway to yield naphthol. Myhre, in the nitration of nitro-2,4,6-tri-*t*-butylbenzene, has observed a partitioning isotope effect due to the same kind of compression.[4]

Saponification of the naphthyl acetate afforded a purple oil, a mixture of compounds as determined by vpc analysis, with carbonyl bands in the ir spectrum. Speculation centered on the tautomeric equilibrium D ⇌ **11** ⇌ E. The naphthol **11** being very crowded by the *peri*-*t*-butyl–hydroxyl interaction could gain some flexibility in ketone forms D and E.



Through several saponification, isolation, and equilibration experiments, the character of the mixture did not seem to be a function of any variable. When acetate **14** was cleaved using 2 equiv of methyl lithium,[12] followed by careful work-up with the exclusion of air, a single colorless compound (vpc), with an ir spectrum free of carbonyl and a uv spectrum having λ_{max}^{EtOH} 329 mμ (log ε 3.46), 322 s (3.48), 315 (3.67), 308 s (3.80), 302 s (3.88), 297 (3.90), 229 (4.68), 215 s (4.48), the pure naphthol **11**, could be obtained. Acetylation of **11** re-formed acetate **14** in high yield. Naphthol **11** is extraordinarily air sensitive and, immediately upon exposure to air, a carbonyl band could be detected in the ir and observable decomposition began. This oxygen sensitivity is similar to the hindered phenol **23**[20] which forms an isolable ketone hydroperoxide **24** under similar conditions.



(11) K. Mislow, J. Borcic, and V. Prelog, *Helv. Chem. Acta*, **40**, 2477 (1957).

(12) C. H. DePuy, G. M. Sappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.* **29**, 2813 (1964).

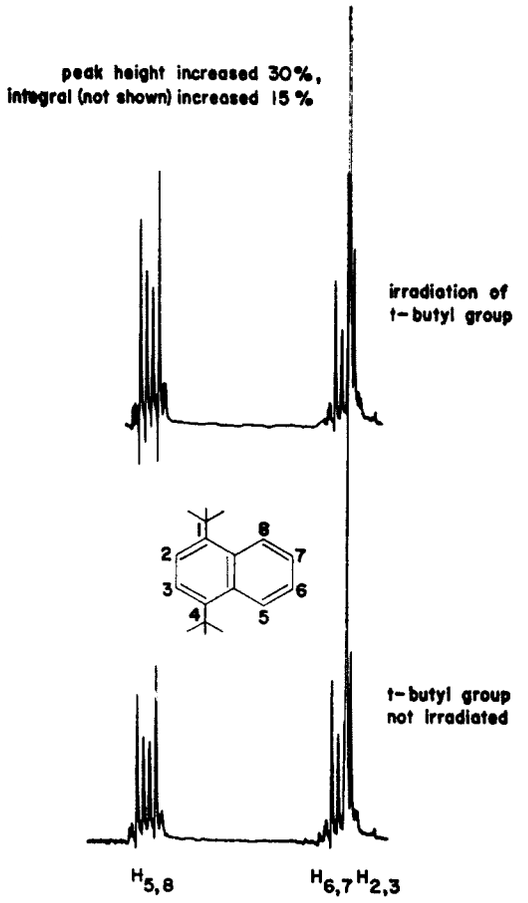


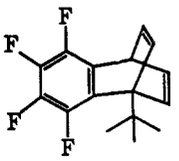
Figure 1.—The nuclear Overhauser effect (NOE) in the nmr spectrum of 1,4-di-*t*-butylnaphthalene detected *via* the increase in intensity of the $H_{5,8}$ signal upon irradiation of the *t*-butyl protons.

Nmr Spectra.—Compressed protons can be detected by nmr spectroscopy. Anet and Winstein[13] have recorded large deshielding shifts when protons in a series of cage compounds were sterically crowded by hydrogen or oxygen atoms. A small shielding effect was detected with an uncompressed proton bonded to a carbon bearing a compressed proton. Nagata[14] has observed moderate compression deshielding in a series of octahydrophenanthrenes. The structural criterion for the observation of this effect appears to be that the distance between the proton in question ("compressee") and the "compressor" atom be significantly less than the sum of their van der Waals radii (2.4 Å in the two-proton case). In our series of compounds, the protons *peri* to the *t*-butyl groups are within this distance. Their resonance positions relative to those of protons in the unsubstituted series are shifted downfield. Table I lists these shifts in parts per million relative to the unsubstituted case. These observations simplify assignments of structure, particularly in the rearranged chloronaphthalene **15** where the presence of two "compressed" protons is unambiguous. Calculations of the bond anisotropy contribution[15] to the deshielding suggest that the net effect averaged over all rotamers is zero or negative. One upfield shift has been observed, H_6 in naphthol **11**, +0.3 ppm relative to α-naphthol. The significance of this is not apparent.

TABLE I
COMPRESSION SHIFTS OF *peri* PROTONS

Compd	Compression shifts, ppm (rel to unsubstituted naphthalenes)
5	0.49
6	0.45
7	0.79
11	0.77
14	0.69
15	0.76 (H 5), 0.83 (H 8)

Another feature of *t*-butyl crowding that has been detected by nmr spectroscopy is the apparent restriction of rotation in the tetrafluoro-*t*-butyl benzbicyclooctatriene **25**.[16] The *t*-butyl absorption, at room



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temperature, was more complex than could be rationalized by long-range coupling to fluorine. The temperature dependence of the complexity also pointed to a rotational barrier as the structural cause. We have not observed such a restricted rotation in our naphthalenes.

Recently, the intramolecular nuclear Overhauser effect has been used for the detection of protons compressed by other protons.[17] This effect can be detected by saturating the "compressor" proton (a double-resonance experiment). Then, the integrated intensity of the "compressee" proton will increase. In the elucidation of the structure and stereochemistry of the ginkolides.[17b] Nakanishi used the Overhauser effect of a *t*-butyl group with great effectiveness. Our *t*-butylnaphthalenes present the necessary structural requirement of compressed protons (as detected by chemical shift effects), thus the nmr experiment was attempted. In the event, with a degassed solution of naphthalene **7**, when the *t*-butyl group was saturated, a 15% increase in the integrated intensity of the *peri* protons was observed (Figure 1).

The *peri*-*t*-butyl group in naphthalenes appears to be a useful probe for the detection of interesting chemical and physical phenomena induced by crowding. Our continuing interest in this field is in the direction of the synthesis of even more-crowded molecules.

Experimental Section[18,19]

5,8-Di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (5).—This scaled-up procedure is taken directly from that used in the

(13) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5249 (1965).

(14) W. Nagata, T. Terasawa, and K. Tori, *ibid.*, **86**, 3746 (1964).

(15) J. W. Ap Simon, W. G. Craig, P. V. DeMarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2339 (1967).

(16) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Comm.*, 27 (1967).

(17) (a) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5250 (1965); (b) M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, *Tetrahedron Letters*, 321 (1967); (c) J. G. Colson, P. T. Lansbury, and F. D. Saeva, *J. Am. Chem. Soc.*, **89**, 4987 (1967).

(18) Melting points were determined on a Fisher-Johns apparatus and are corrected. Infrared spectra were obtained with a Perkin-Elmer Infracord. Ultraviolet spectra were determined using a Cary 15 spectrophotometer. Nmr spectra were obtained with a Varian A-60 instrument using TMS (δ 0.00) as a standard. A nitrogen atmosphere was maintained over all reactions by using the apparatus described by Johnson and Schneider.[19] Analyses were done by Spang Microanalytical Laboratory.

(19) W. S. Johnson and W. P. Schneider, *Org. Syn.*, **30**, 18 (1950).

mechanistic study of the reaction.[5] A 100-ml methylene chloride solution of 10.0 g (48.7 mmoles) of 2,5-di-*t*-butylaniline and 4.96 g (48.7 mmoles) of pivalic acid was added over a 1-hr period to a refluxing solution of 5.52 g (53.6 mmoles) of *n*-butyl nitrite and 9.94 g (146 mmoles) of furan in 100 ml of methylene chloride. After addition was complete, the mixture was refluxed for 1 hr. The reaction mixture was then washed with 300 ml of saturated aqueous sodium bicarbonate. The methylene chloride layer was then dried with sodium sulfate, the solvent was evaporated, and the residue was chromatographed on 200 g of silica gel. Hexane and 1:1 hexane–benzene elution removed other products; and the benzene fractions gave 4.55 g of material which was evaporatively distilled. The distillate was recrystallized from pentane to afford 2.73 g (21%) of adduct: mp 115–116°; ir, λ_{max} (CS_2) 13.95 μ; nmr (CCl_4), δ 1.30 (*t*-butyl), 5.95 (m) (H_1, H_4), 6.77 (s) (H_6, H_7), 6.87 (m) (H_2, H_4).

5,8-Di-*t*-butyl-1,2,3,4-tetrahydronaphthalene-1,4-endoxide (6).—In a semimicro hydrogenation apparatus, a solution of 1.50 g (5.85 mmoles) of furan adduct in 60 ml of methanol was treated with 200 mg of 10% palladium on carbon and hydrogenated at 26° and atmospheric pressure. Hydrogen uptake (141 ml) was complete in 30 min. The catalyst was filtered and the solvent was evaporated affording a quantitative yield of white crystalline hydrogenation product: mp 134.5–135.5°; nmr (CCl_4), δ 1.37 (s) (*t*-butyl), 1.37 and 2.00 (m) (H_2, H_3; *endo*, *exo*), 5.66 (dd, J = 3.0 and 1.7 cps) (H_1, H_4), 7.02 (s) (H_5, H_7). An analytical sample, mp 134.5–135.5°, was prepared by recrystallization from methanol.

Anal. Calcd for: C, 83.7; H, 10.1. Found: C, 83.8; H, 10.0.

1,4-Di-*t*-butylnaphthalene (7).—A solution of 500 mg (1.94 mmoles) of endoxide in 10 ml of ethanol saturated with anhydrous hydrogen chloride was refluxed for 64 hr. The solvent was removed under vacuum and the solid residue was recrystallized from ethanol to afford 437 mg (94%) of the naphthalene: mp 61–62°; uv, $\lambda_{max}^{isooctane}$ 214 mμ (log ϵ 4.73), 221 (4.90), 256 (3.36), 267 (3.65), 276 (3.86), 286 (3.96), 298 (3.81), 316 (2.72); nmr (CCl_4), δ 1.61 (s) (*t*-butyl), 7.37 (s) (H_2, H_3), 7.39 (dd, J = 6.8 and 3.6 cps) (H_6, H_7), 8.50 (dd, J = 6.8 and 3.6 cps) (H_5, H_8).

Anal. Calcd for $C_{18}H_{24}$: C, 89.9; H, 10.1. Found: C, 89.8; H, 10.2.

Rearrangement of 5,8-Di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (5).—A solution of 500 mg (1.95 mmoles) of furan adduct in 10 ml of ethanol saturated with anhydrous hydrogen chloride was refluxed for 30 min. The solvent was then evaporated under vacuum and 10 ml of acetic anhydride and ten drops of pyridine were added to the residue. This solution was refluxed for 5 hr, then it was cooled and added to ice–water and allowed to stand to permit hydrolysis of the excess anhydride. The resulting aqueous mixture was extracted with 15 ml of hexane. The hexane was washed with water and dried with sodium sulfate. The residue remaining after solvent removal was chromatographed on 15 g of silica gel. Hexane elution afforded crude **2-chloro-5,8-di-*t*-butylnaphthalene (15)** which was recrystallized from pentane to afford 86 mg (16%) of material: mp 92–93.5°; uv, $\lambda_{max}^{isooctane}$ 214 mμ (log ϵ 4.37), 232 (4.70), 257 (s) (3.23), 267 (s) (3.47), 278 (3.67), 284 (s) (3.68), 289 (3.74), 294 (3.62), 299 (3.56), 308 (s) (2.96), 316 (s) (2.61), 323 (2.70); nmr (CCl_4), δ 1.55 (s), 1.57 (s) (*t*-butyl), 7.31 (s) (H_2, H_3), 7.30 (dd, J = 9.5 and 2.3 cps) (H_6); 8.37 (d, J = 9.5 cps) (H_5); 8.44 (d, J = 2.3 cps) (H_8). The sample prepared for analysis by two recrystallizations from pentane had mp 92.5–93.5°.

Anal. Calcd for $C_{18}H_{23}Cl$: C, 78.7; H, 8.4; Cl, 12.9. Found: C, 78.9; H, 8.3; Cl, 12.8.

Elution with benzene yielded crude **1-acetoxy-5,8-di-*t*-butylnaphthalene (14)** which was evaporatively distilled to afford 330 mg (57%) of a solid: mp 101–102°; ir, λ_{max} (CS_2) 5.64 μ; uv, $\lambda_{max}^{isooctane}$ 210 mμ (log ϵ 4.32), 231 (4.73), 258 (s) (3.78), 292 (3.89), 303 (s) (3.77), 323 (s) (2.96); nmr (CCl_4), δ 1.55 (s), 1.58 (s) (*t*-butyl), 2.26 (s) (acetyl methyl), 7.39 (m) (H_2, H_3, H_6, H_7), 8.32 (dd, J = 7.9 and 2.4 cps) (H_5). An analytical sample, mp 101–102°, was prepared by recrystallization from pentane.

Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.5; H, 8.8. Found: C, 80.5; H, 8.7.

5,8-Di-*t*-butyl-1,4-dideuterio-1,4-dihydronaphthalene-1,4-endoxide (5-d_2). A. Furan-2,5-dicarboxylic Acid.—A mixture of 100 g (476 mmoles) of powdered mucic acid and 300 ml of fuming hydrobromic acid was refluxed for 20 hr. Upon cooling, a solid was filtered off. The furandicarboxylic acid was leached from the solid with 500 ml of 95% ethanol. The ethanol was removed under vacuum and the tarry residue was triturated with 50 ml of monoglyme to remove tars. The remaining dark solid (17% yield) has an ir spectrum identical with that of samples of higher purity. The solid was recrystallized from dimethylformamide–water to afford colorless material in 8% yield having ir, λ_{max} (KBr) 3.0–4.1, 5.89, 11.6, and 13.2 μ (furan ring). Recrystallization of the above diacid from dimethylformamide–deuterium oxide gave diacid-O-d_2[20] having ir, λ_{max} (KBr) 3.8–5.0, 5.88, 11.6, and 13.2 μ.

B. 2,5-Dideuteriofuran.—A mixture of 4.22 g (26.7 mmoles) of furan-2,5-dicarboxylic acid-O-d_2, 10 g of quinoline, and 0.1 g of cupric oxide was heated in an oil bath at 200° (bath temperature; the temperature was gradually raised to 280°. The evolving gases were passed through a column of sodium hydroxide pellets to remove CO_2. The column was kept at 50–60° to prevent furan condensation. The vapor train was then passed through a water-cooled condenser and collected in a flask cooled in a Dry-Ice–acetone bath, to afford 510 mg (27%) of furan. The nmr integral of the 2,5 protons was 45% of the 3,4 protons.

C. 5,8-Di-*t*-butyl-1,4-dideuterio-1,4-dihydronaphthalene-1,4-endoxide (5-d_2).—The standard procedure was employed to afford an adduct of mp 113°, whose mass spectrum showed the following molecular ion peak ratio (after correction for C^{13} natural abundance): d_0, 15.3%; d_1, 42.3%; d_2, 35.0%; d_3, 6.5%; d_4, 0.9%.[21]

Study of Isotope Effect in the Rearrangement of Deuterated Adduct.—A 110-mg sample of protio adduct and a 110-mg sample of deuterio adduct were simultaneously refluxed with 2-ml portions of the same batch of ethanol saturated with anhydrous hydrogen chloride, following the procedure described above. After removal of solvent from this step, the two residues were treated with acetic anhydride and pyridine as before. The acetic anhydride–pyridine solutions were directly analyzed by gas chromatography using a calibration curve prepared by the analysis of synthetic mixtures of chloronaphthalene **15** and acetoxynaphthalene **14** in acetic anhydride solutions. The observed yields in the protio sample were 72.3% acetate and 16.1% chloro compound, while the deuterated sample afforded 57.3% acetate and 28.8% chloro compound.

5,8-Di-*t*-butyl-1-naphthol (11).—A solution of 200 mg (0.67 mmole) of acetoxy compound **14** in 5 ml of ether under a nitrogen atmosphere was treated with 1 ml of a 5% solution of methyllithium in ether. The solution was stirred at 25° for 1 hr at which point a solution of 100 mg (1.87 mmoles) of ammonium chloride in 3 ml of water was added to the reaction. The ether layer was separated and dried with sodium sulfate. Upon removal of the ether, an oil was obtained which was evaporatively distilled (150°, 0.02 mm) to afford 168 mg (98%) of the naphthol as an oil: ir, λ_{max} (CS_2) 2.80, 3.02 μ; uv, $\lambda_{max}^{isooctane}$ 215 mμ (s) (log ϵ 4.48), 228 (4.68), 297 (3.90), 302 (s) (3.88), 308 (s) (3.80), 315 (3.67), 322 (s) (3.49), 329 (3.46); nmr (CCl_4), δ 1.55 (s), 1.58 (s) (*t*-butyl), 5.11 (s) (OH), 6.45 (m) (H_2), 7.26 (m) (H_3, H_6, H_7), 7.99 (m) (H_4). A satisfactory elemental analysis of this oil could not be obtained. When the naphthol was kept in a nitrogen atmosphere, its ir spectrum appeared to be unchanged. However, upon exposure to air, the naphthol converted to a substance, ir, λ_{max} (CS_2) 5.7–6.0 μ, which appeared to be a ketone hydroperoxide.

Acetylation of 5,8-di-*t*-butyl-1-naphthol (11).—A solution of 67 mg (0.26 mmole) of freshly prepared naphthol, 5 ml of acetic anhydride, and 15 drops of pyridine was refluxed for 3 hr. After the acetic anhydride was decomposed with water, the organic material was extracted with hexane, the hexane was dried, then evaporated to yield a crude product which was evaporatively distilled to afford 61 mg (78%) of acetoxy compound **14**, mp 101–102°, ir spectrum superimposable on that of an authentic sample.

Registry No.—**5**, 10565-41-0; **6**, 10565-42-1; **7**, 10565-10-3; **11**, 15188-44-0; **14**, 15161-80-5; **15**, 15161-81-6; **21**, 15188-47-3; **22**, 6142-88-7; **5-d_2**, 15188-29-1.

(20) These procedures were adapted from descriptions in *Beilstein*, **18**, 328 (1900) (saccharic acid to furandicarboxylic acid), and from E. C. Wagner and J. K. Simons, *J. Chem. Ed.*, **13**, 270 (1936) (furoic acid to furan).

(21) Morgan-Schaffer Corp., Montreal 26, Que., obtained this spectrum.

Acknowledgment.—We thank Professor Nakanishi for stimulating our interest in the Overhauser effect during his tenure as New York State Science and Technology Foundation Distinguished Visiting Professor at Fordham, and we thank Professor Kenneth Williamson for performing the NOE experiment.

Fluoroketenes. II.[1] Difluoroketene

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Received June 16, 1967

Difluoroketene, as obtained by zinc dehalogenation of bromodifluoroacetyl halides, is a reactive and unstable compound. The ketene itself has not been detected except by its dissociation at 35° to form carbon monoxide and tetrafluoroethylene and by trapping reactions. With excess bromodifluoroacetyl chloride it forms a vinyl ester, 1-chloro-2,2-difluorovinyl bromodifluoroacetate, and with acetone it forms α,α-difluoro-β,β-dimethylpropiolactone.

Dehalogenation of haloacetyl halides by zinc has recently been used successfully to prepare both dichloro-[2] and dibromoketene.[3] The preparation of difluoroketene in ether solution by zinc dehalogenation of chlorodifluoroacetyl bromide has also been reported,[4a] but the evidence for its existence is inconclusive.[4b] We now wish to report our findings on the subject, which indicate that difluoroketene is a highly reactive, short-lived material.

The finding of a convenient synthetic route to bromodifluoroacetyl halides furnished starting materials which are probably more easily dehalogenated than the chlorodifluoroacetyl derivatives used previously.[4a] The new three-step synthesis starts with a displacement of fluoride from tetrafluoroethylene by sodium methoxide at 60° and a few atmospheres of pressure to form the known methyl trifluorovinyl ether. This unsaturated ether reacts readily with bromine to give a material assumed to be the simple dibromo adduct, but which tends to liberate free bromine. The last step is an unusual and facile cleavage of the ether group by chlorosulfonic acid to give the acid halide function. This cleavage, which proceeds under much milder conditions than the more conventional reaction with sulfuric acid, is a useful general reaction as will be further illustrated in future publications.

$$CF_2{=}CF_2 \xrightarrow{NaOCH_3} CF_2{=}CFOCH_3 \xrightarrow{Br_2} BrCF_2CFBrOCH_3 \xrightarrow{ClSO_3H} BrCF_2\overset{O}{\overset{\|}{C}}X \quad (X = Cl, Br)$$

Results of dehalogenations of bromodifluoroacetyl chloride and bromide with zinc in ether indicate that difluoroketene or some form of it complexed with zinc halide is formed, and that it is very short-lived, even at the lowest possible reaction temperature (−5 to 0°). An ether solution resulting from such a low-temperature dehalogenation of bromodifluoroacetyl chloride, when kept cold and examined by infrared, showed no characteristic ketene band. Bands were observed for a vinyl ester **1** (X = Cl), and this compound could be separated in low yield by gas chromatography from the complex mixture of products. Compound **1** could be formed by reaction of difluoroketene with the starting material, bromodifluoroacetyl chloride. Another purified product showed very similar infrared and nmr spectra and had an empirical formula corresponding to 3 moles of difluoroketene to one of the acid chloride. A still higher boiling oil showed similar infrared and nmr spectra and contained more fluorine and less chlorine and bromine. Yields of isolated products were quite low, and some carbon monoxide was evolved. At a higher temperature (*ca.* 35°) much more carbon monoxide was evolved, and tetrafluoroethylene was detected. These two products are best accommodated by assuming the presence of free difluoroketene, which decomposes to CO and CF_2. The carbene could undergo a number of reactions, one of which is the known dimerization to form tetrafluoroethylene.

$$BrCF_2\overset{O}{\overset{\|}{C}}X \xrightarrow[\text{ether, } <0°]{Zn} [CF_2{=}C{=}O] \xrightarrow{BrCF_2COX} CF_2{=}CX\overset{O}{\overset{\|}{O}}CCF_2Br$$

1 (X = Br, Cl) + other products

$$[CF_2{=}C{=}O] \xrightarrow{35°} CO + [CF_2{:}] \longrightarrow CF_2{=}CF_2$$

The earlier evidence[4a] for the existence of difluoroketene rested mainly on the isolation of difluoroacetamide in low yield when an ether solution distilled from a zinc dehalogenation reaction was treated with ammonia. We have confirmed this reaction, but feel it is not convincing evidence, since difluoroacetamide could also result from the action of ammonia on a vinyl ester like **1** or on a product of reductive dehalogenation by zinc.[5] Yields of difluoroacetyl derivatives are not necessarily low, since we have further shown that difluoroacetic acid can be obtained in 52% yield by addition of water directly to the reaction mixture from zinc and bromodifluoroacetyl chloride. Reaction in methyl formate provided an indication that at least a portion of these difluoroacetyl derivatives are derived from zinc reduction products. With

(1) For paper I, see D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 5582 (1966).

(2) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

(3) W. T. Brady, *ibid.*, **31**, 2676 (1966).

(4) (a) N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *J. Gen. Chem. USSR*, **27**, 2832 (1957). (b) R. E. Banks, R. N. Haszeldine, and D. R. Taylor [*J. Chem. Soc.*, 5602 (1965)] refer to some unpublished work by J. M. Birchall, R. N. Haszeldine, and M. Jefferies, who were unable to repeat this synthesis of difluoroketene.

(5) Yu. A. Cheburkov, E. I. Mysov, and I. L. Knunyants [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1570 (1963)] describe the formation of reduction products from related α-bromoperfluoroacid halides and zinc.