NMR (CCl_4) δ 7.32 (d, J = 6.0 Hz, 1 H), 5.90 (d, J = 6.0 Hz, 1 H), 2.4-1.1 (m, 11 H), 1.00 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.0 (s), 170.9 (d), 129.2 (d), 66.5 (s), 57.4 (s), 49.4 (d), 36.4 (t), 33.2 (t), 32.2 (t), 29.0 (t), 27.3 (t), 19.3 (q). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.83; H, 9.25.

(1*R,5*S**,8*S**)-5-Methyltricyclo[6.3.0.0^{1,5}]undecan-4-one (17).** A mixture of 1.05 g (5.95 mmol) of **16** and a catalytic amount of 10% palladized carbon in 90 mL of ethyl acetate was stirred at room temperature for 2 h under 1 atm of H_2. After filtration, the filtrate was concentrated and flash chromatography (elution with ether/petroleum ether, 3:97) of the crude product gave 0.93 g (88% yield) of **17**: mp 58-60 °C; IR (KBr) 1730 cm^{-1}; MS m/e 178 (M^+, 86), 122 (82), 121 (100), 107 (70); ^1H NMR (CCl_4) δ 2.4-1.1 (m, 15 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 226.6 (s), 60.6 (s), 58.8 (s), 51.3 (d), 37.8 (t), 37.3 (t), 36.1 (t), 35.9 (t), 32.7 (t), 31.8 (t), 27.1 (t), 17.0 (q). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.56; H, 10.23.

(1*R,5*R**,8*S**)-8-Methyltricyclo[6.4.0.0^{1,5}]dodecan-9-one (18).** To a solution of LDA (6.50 mmol) in 5 mL of dry THF was added dropwise a solution of 930 mg (5.22 mmol) of **17** in 6 mL of dry THF at -78 °C during 6 min under N_2. The solution was stirred at -78 °C for 1 h and 1.33 mL (10.4 mmol) of trimethylsilyl chloride was added. The mixture was warmed to room temperature and stirred at that temperature for 2 h. The mixture was filtered and the filtered solid was washed with petroleum ether. The combined filtrate was concentrated to give the residue, which was diluted with petroleum ether. The mixture was filtered again. The filtration was repeated until the filtrate became a clear solution to give the crude silyl enol ether: IR (neat) 3050, 1645, 1255, 845 cm^{-1}.

To a solution of the above enol ether in 15 mL of hexane was added 1.20 mL (11.7 mmol) of diethylzinc at room temperature under N_2. To the solution was added dropwise 1.26 mL (15.7 mmol) at diiodomethane during 30 min. The mixture was stirred at room temperature for 2 h and cold NH_4Cl solution was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phase was washed with $NaHCO_3$ solution and brine and dried ($MgSO_4$). Evaporation of the solvent gave the crude siloxycyclopropane: IR (neat) 3030, 1245, 830 cm^{-1}.

To a solution of 2.55 g (15.7 mmol) of anhydrous $FeCl_3$ in 11 mL of dimethylformamide was added dropwise a solution of the above cyclopropane and 0.46 mL (5.74 mmol) of pyridine in 11 mL of the same solvent at 0 °C during 30 min under N_2. The solution was stirred at 0 °C for 10 min and then at room temperature for 3 h. Cold 5% HCl was added and then the mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave the crude ring-expanded chloride: IR (neat) 1700 cm^{-1}.

A mixture of the above chloride and 4.28 g (52.2 mmol) of sodium acetate in 50 mL of MeOH was stirred at reflux for 7 h. After evaporation of the solvent, water was added. The mixture was extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by the column chromatography (elution with ether/petroleum ether, 2:98) of the crude product gave 107 mg of recovered **17** and 225 mg (26% yield from **17**) of the enone: IR (neat) 1670 cm^{-1}: MS m/e 190 (M^+, 13), 122 (100), 107 (59): ^1H NMR ($CDCl_3$) δ 6.9-6.6 (m, 1 H), 5.95 (d, J = 9.8 Hz, 1 H), 2.4-1.1 (m, 13 H), 1.05 (s, 3 H).

Hydrogenation of 209 mg (1.10 mmol) of the above enone for 1 h as described above gave 195 mg (93% yield) of **18** after flash chromatography (elution with ether/petroleum ether, 3:97): IR (neat) 1700 cm^{-1}; MS m/e 192 (M^+, 100), 124 (69), 121 (94), 108 (52), 93 (54); ^1H NMR ($CDCl_3$) δ 2.7-1.1 (m, 17 H), 1.08 (s, 3 H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.87; H, 10.53.

(1*S,5*S**,8*S**)-8-Methyltricyclo[6.4.0.0^{1,5}]dodecane (19). Method A. Wolff-Kishner Reduction of 12.** A solution of 220 mg (1.15 mmol) of **12**, 450 mg (8.02 mmol) of KOH, and 0.70 mL (11.5 mmol) of 80% hydrazine hydrate in 5 mL of diethylene glycol was refluxed at ca. 150 °C for 3 h. Excess hydrazine and water were distilled off and the solution was heated at 210 °C for 4 h. The cooled solution was neutralized with 5% HCl and the mixture was extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with petroleum ether) of the crude product gave 133 mg (65% yield) of **19**: IR (CCl_4) 2930, 2850, 1450, 1370 cm^{-1}; MS m/e 178 (M^+, 23), 163 (45), 135 (100); ^1H NMR ($CDCl_3$) δ 2.2-1.0 (m, 19 H), 0.95 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 56.5 (s), 44.4 (d), 43.4 (s), 39.9 (t), 36.9 (t), 36.7 (t), 34.0 (t), 32.4 (t), 30.1 (t), 24.5 (t), 23.4 (t), 22.5 (t), 21.4 (q). Anal. Calcd for $C_{13}H_{22}$: C, 87.56: H, 12.44. Found: C, 87.65; H, 12.52.

Method B. Wolff-Kishner Reduction of 18. Reduction of 177 mg (0.92 mmol) of **18** as described above gave 108 mg (66% yield) of a hydrocarbon whose ^{13}C NMR spectrum is identical with that of **19** obtained by method A.

Acknowledgment. Thanks are due to the Analytical Center, Faculty of Engineering, Osaka University, for assistance in obtaining NMR and mass spectra on JEOL JNM-GSX-400 and JEOL JMS-DX303 spectrometers and the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of facilities for the X-ray analysis.

Registry No. (±)-**9**, 40573-28-2; (±)-**10**, 130436-25-8; (±)-**11**, 130605-59-3; (±)-**12**, 130436-26-9; (±)-**13**, 130436-27-0; (±)-**14**, 130436-28-1; (±)-**15**, 119972-39-3; (±)-**16**, 130548-52-6; (±)-**17**, 130436-29-2; (±)-**18**, 130436-30-5; (±)-**19**, 130436-31-6.

Supplementary Material Available: Details of X-ray crystallographic analysis of **14** and Tables I-III listing the bond lengths, bond angles, atomic coordinates, and anisotropic parameters of **14** (8 pages). Ordering information is given on any current masthead page.

Two Dimers Derived from the 2,4,6-Tri-*tert*-butylphenyl Radical, Formed during Reactions of the Aryllithium or the Grignard Reagent with Carbonyl Compounds

Joseph Frey, David A. Nugiel, and Zvi Rappoport*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received May 11, 1990

The 2,4,6-tri-*tert*-butylphenyl radical **1**• was generated from 1-bromo-2,4,6-tri-*tert*-butylbenzene (**1**-Br) with Me_3Sn•, and its isomeric radical 3,5-di-*tert*-butylneophyl **2**• from photolysis of 1,3,5-tri-*tert*-butylbenzene (**1**-H) with *t*-BuOOBu-*t*, and their ESR spectra were measured.[1] On raising the temperature in the **1**•-forming reaction, **2**• is observed, and from the kinetics of the decay of both species, eq 1 was suggested, where $(2)_2$ is a dimer that was

$$1^\bullet \xrightarrow{\text{isom}} 2^\bullet \rightarrow (2)_2 \qquad (1)$$

not isolated or identified. For **1**• at 25 °C log ($\tau_{1/2}$/s) = -2.2.[1a,c] On thermal decomposition of *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate, the ESR spectrum of **2**• was also observed,[2] and only methyl 2,4,6-tri-*tert*-butylbenzoate was identified after CH_2N_2 treatment. In spite of the known neopentyl radical rearrangement,[3] the rearranged radical **3**• was not observed under these conditions.[4]

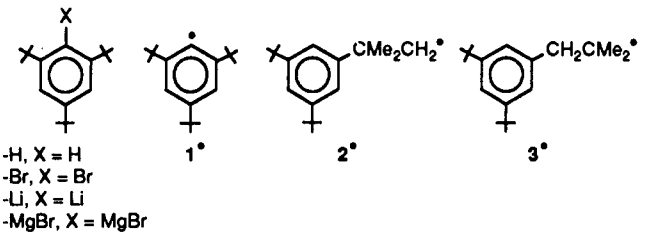
(1) (a) Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 3011. (b) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *Ibid.* **1976**, *98*, 6803. (c) For a review of persistent carbon stable radicals, see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *109*, 13.

(2) Icli, S.; Kandil, A. K.; Thankachan, C.; Tidwell, T. T. *Can. J. Chem.* **1975**, *53*, 979.

(3) Hamilton, E. J., Jr.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795.

(4) It was quoted in ref 1b that **3**• is formed from **2**•, according to ref 3 and to Maillard, B.; Ingold, K. U. (*J. Am. Chem. Soc.* **1976**, *98*, 1224), but only rearrangements of related radicals were reported.

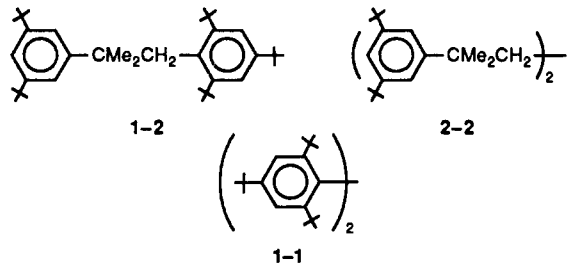
0022-3263/91/1956-0466$02.50/0



1-H, X = H
1-Br, X = Br
1-Li, X = Li
1-MgBr, X = MgBr

1• 2• 3•

(2,4,6-Tri-*tert*-butylphenyl)lithium (1-Li) reacts as a nucleophile toward phosphorus electrophiles,[5] and CO_2[2,6] and acts as a base toward silane,[7a] benzyl methyl ketone,[7b] or THF[7b] and presumably toward acetone and acetophenone.[7c] However, in spite of its instability "at higher temperatures"[4] (presumably >0 °C), homolytic dissociation of 1-Li or 1-MgBr or a single electron transfer (SET) during reaction with electrophilic substrates to give radical 1• or 2• was not reported. We report here that 1-Li or 1-MgBr gave dimers 2-2 and 1-2 but not dimer 1-1 with acyl halides or esters.



1-2 2-2

1-1

Results and Discussion

On attempted substitution of the halogen of several acyl halides or the ethoxy group of diethyl oxalate by the bulky 1-Li and 1-MgBr, the substitution products were formed in a very low yield or not at all, and the main products were the dimers 1-2 and 2-2 and the hydrolysis product 1-H. Reaction of 1-MgBr with diphenylacetyl chloride gave a 35% yield of 2,5-bis(3,5-di-*tert*-butylphenyl)-2,5-dimethylhexane (2-2) and none of the expected triarylethanone (eq 2).[8]

$$Ph_2CHCOCl + 2,4,6\text{-}t\text{-}Bu_3C_6H_2MgBr \xrightarrow[\text{toluene}]{\text{ether}} \mathbf{2\text{-}2} \quad (2)$$

Reaction of 1-Li was performed with oxalyl chloride (4), methyl chloroglyoxylate (5), and diethyl oxalate (6). The most reactive compound, 4, reacted already at −78 °C and gave the unsymmetrical dimer 1-(2,4,6-tri-*tert*-butylphenyl)-2-(3,5-di-*tert*-butylphenyl)-2-methylpropane (1-2) and low yields of 2,4,6-tri-*tert*-butylbenzoic acid[6b] by displacement of a single chlorine, followed by decarbonylation, and bis(2,4,6-tri-*tert*-butylphenyl) diketone,[9] by substitution of both chlorines. Reaction of 6 at 0 °C gave only dimer 2-2. In the reaction of 5 at −78 °C only 1-2 was formed after 1 or 24 h, whereas at −10 °C, a 1:1.5 ratio of 1-2:2-2 was formed (Scheme I) together with methyl (2,4,6-tri-*tert*-butylphenyl)glyoxylate. At room temperature the main product after workup was 1-H.

Reaction of 1-Li with $CuCl_2$ or $CuBr_2$, a procedure that gave the corresponding biphenyl from (tetramethylphenyl)- and (pentamethylphenyl)lithium,[10] gave 1-Cl and

Scheme I

XCOCOY	+ ArLi	→ 1-2 + $ArCO_2H$ + ArCOCOAr
4: X = Y = Cl	(−78 °C)	1-2
5: X = Cl; Y = OMe	(−78 °C)	1-2 + 2-2
6: X = Y = OEt	(−10 °C)	2-2 + $ArCOCO_2Et$
	(0 °C)	Ar = 2,4,6-*t*-$Bu_3C_6H_2$

Table I. Selected Bond Lengths and Angles for 1-2

bond, Å	struct. 1	struct. 2
C(1)–C(2)	1.58 (1)	1.585 (9)
C(1)–C(9)	1.55 (1)	1.544 (9)
C(1)–C(15)	1.55 (1)	1.56 (1)
C(1)–C(16)	1.54 (1)	1.54 (1)
C(2)–C(3)	1.516 (9)	1.518 (9)
C(4)–C(17)	1.562 (9)	1.56 (1)
C(8)–C(25)	1.58 (1)	1.58 (1)
C(6),C(13),C(25)–C_{sp^3}	1.54 (1)–1.55 (1)	1.52 (1)–1.55 (1)
4C=C[a]	1.38 (9)–1.405 (9)	1.38 (1)–1.40 (1)
4C=C[b]	1.38 (1)–1.396 (9)	1.36 (1)–1.41 (1)
C(3)–C(4)	1.439 (9)	1.44 (1)
C(3)–C(8)	1.413 (9)	1.430 (9)
C(17)–Me	1.52 (1)–1.56 (1)	1.54 (1)–1.56 (1)
C(21)–Me	1.54 (1)–1.55 (1)	1.47 (2)–1.53 (2)
C(25)–Me	1.54 (1)–1.56 (1)	1.54 (1)–1.55 (1)
C(29)–Me	1.50 (1)–1.51 (1)	1.40 (2)–1.46 (2)
C(33)–Me	1.48 (2)–1.52 (2)	1.49 (2)–1.52 (1)

angle, deg	struct. 1	struct. 2
C(4)–C(5)–C(6)	124.1 (6)	124.9 (7)
C(5)–C(6)–C(7)	115.7 (6)	116.3 (7)
C(6)–C(7)–C(8)	123.8 (7)	122.2 (7)
C(7)–C(8)–C(3)	118.8 (6)	120.1 (6)
C(8)–C(3)–C(4)	117.6 (6)	116.6 (6)
C(3)–C(4)–C(5)	117.7 (6)	116.9 (6)
C–C–C[a]	117.8 (6)–121.8 (7)	118.6 (7)–120.8 (7)
6C–C(29)–C	103.7 (8)–112.9 (7)	104–116
6C–C(33)–C	102 (1)–114.0 (9)	107.1 (9)–112 (9)
6C–C(1)–C	104.6 (8)–113.8 (6)[c]	104.0 (6)–113.4 (5)[c]
6C–C(4)–C	107.9 (6)–112.5 (6)	104.7 (9)–114.3 (9)
6C–C(17)–C	104.3 (6)–117.0 (6)[d]	106.2 (9)–118.1 (6)[d]
6C–C(25)–C	104.6 (6)–118.3 (6)[e]	105.1 (7)–115.2 (6)[f]

[a] In the tetrasubstituted ring. [b] In the trisubstituted ring. [c] The wider angle is C(16)–C(1)–C(2). [d] The wider angle is C(4)–C(17)–C(19). [e] The wider angle is C(8)–C(25)–C(28). [f] The wider angle is C(8)–C(25)–C(27).

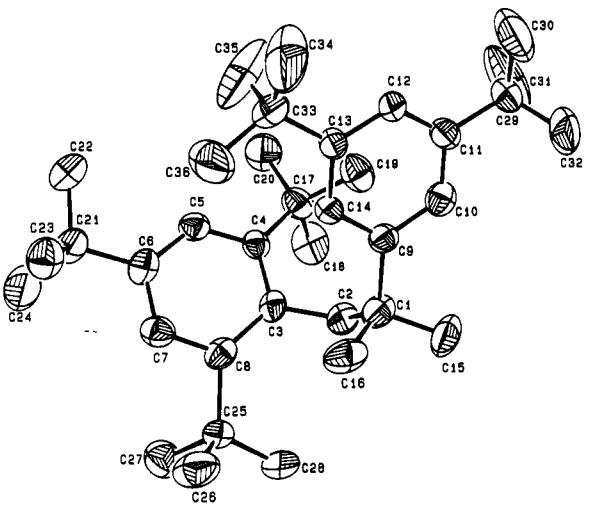


Figure 1. ORTEP drawing and atom numbering for 1-2, structure 1.

(5) (a) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587; **1982**, *104*, 6167. Yoshifuji, M.; Shibayama, K.; Inamoto, T.; Matsushita, T.; Nishimoto, K. *Ibid.* **1983**, *105*, 2495. (b) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1985**, *26*, 1727. (c) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809. (d) Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1984**, 689.

(6) (a) Betts, E. E.; Barclay, L. R. C. *Can. J. Chem.* **1955**, *33*, 672, 1768. (b) Barclay, L. R.; Sonawane, H. R.; MacDonald, M. C. *Ibid.* **1972**, *50*, 281.

(7) (a) Oehme, H.; Weiss, H. *J. Organomet. Chem.* **1987**, *319*, C16. (b) Yoshifuji, M.; Nakamura, T.; Inamoto, N. *Tetrahedron Lett.* **1987**, *28*, 6325. (c) Nakamura, T.; Choi, Y. J.; Yoshifuji, M.; Inamoto, N. "Abstracts of Papers", 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. 2L42, quoted in ref 9.

(8) In contrast, 20-h reflux of 1-Li with dimesitylketene gave after aqueous workup only dimesitylacetic acid, from hydrolysis of the ketene and 1-H.

(9) Staab, H. A.; Lauer, D. *Chem. Ber.* **1968**, *101*, 864.

1-Br, respectively, but no dimer.

Since 1-2 is crowded according to space filling models, and it shows an unexpectedly (and yet unaccountable) high absorption at λ_{max} 238 nm (shoulder), (ϵ = 9300), the possibility of homolysis in solution was investigated. No reaction of 1-2 in hexane after 70 h at 20 °C or in hexachlorobutadiene after 60 h at 120 °C was observed. In contrast, after 2 days in refluxing *n*-decane several unidentified products that may result from C-C bond cleavage and further reactions were formed.

Solid State Structure of 1-2. The high absorption of 1-2 at 238 nm could reflect a distortion of the aromatic ring(s) or an unusual interaction between the rings. Hence, its X-ray diffraction was determined. Important structural features are given in Table I. Other structural, positional and thermal parameters are given in supplementary tables S1-S5. The ORTEP drawing with atom labeling is shown in Figure 1, stereoscopic views of two crystallographically independent molecules are given in supplementary figures S1 and S2, and the unit cell in figure S3.

Two slightly crystallographically different molecules were found in the unit cell. Figures 1, S1, and S2 show large elongated ellipsoids of the methyls of the two *t*-Bu groups on the trisubstituted ring and of one *t*-Bu group (C(21)-C(24)) on the tetrasubstituted ring, indicating an extensive thermal motion.

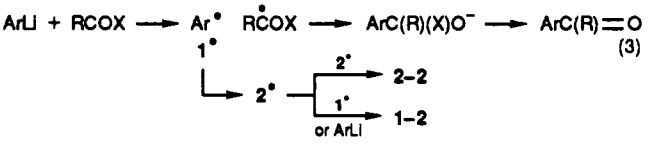
The high steric hindrance is only partially revealed in the X-ray structure. In the trisubstituted ring the C=C bond lengths of 1.38-1.405 Å and bond angles of 117.8° (C(14)-C(9)-C(11))-121.8° (structure 2) are normal. The ring carbons deviate from the average ring plane by only 0.074 Å and 0.039 Å in structures 1 and 2, respectively. Bond angles to and around the two *t*-Bu groups are close to tetrahedral with some deviations of several degrees. Bond lengths within one *t*-Bu group are normal but short C-Me bond lengths of 1.40-1.46 Å were encountered for the other *t*-Bu group ((C29)-C(32)) in structure 2.

The steric effects are reflected more in the tetrasubstituted ring. Four intraring bond lengths are normal (ca. 1.39 Å in structure 1 and 1.36-1.41 Å in structure 2), but the two bonds that are part of the 1,2,3-trisubstituted system are elongated: C(3)-C(8) = 1.413 Å and 1.43 Å and C(3)-C(4) = 1.439 Å and 1.44 Å in structures 1 and 2, respectively. The two bonds to the *t*-Bu groups elongate appreciably from the sp^2-sp^3 value of 1.50 Å to 1.56 Å (C(4)-C(17)) and 1.58 Å (C(8)-C(25)). The three interring C-C-C bond angles at the crowded center (C(7)-C(8)-C(3); C(8)-C(3)-C(4); C(3)-C(4)-C(5)) are 117.7-118.8° in structure 1, 116.6-120.1° in structure 2, and C(5)-C(6)-C(7) = 115.7° and 116.3°, whereas C(4)-C(5)-C(6) widens to 124.1° and 124.9°. The C(3)-C(8)-C(25) angle opens to 128.9° and 122.6° (structures 1 and 2) and C(3)-C(4)-C(17) opens to 123.8° and 128.5° (structures 1 and 2), in order to relieve steric interactions between ortho substituents. Deviations of the ring carbons from the average ring plane average 0.053 Å and 0.063 Å for structures 1 and 2, but C(3) is 0.099 Å above (structure 1) and 0.108 Å below (structure 2) this plane.

The dihedral angles between the two rings are 34.24° (structure 1) and 39.74° (structure 2). The intermolecular dihedral angles in the unit cell are 10.45° and 0.91° between the two trisubstituted rings and are 40.61° and 33.39° between the two tetrasubstituted rings. The trisubstituted rings of the two crystallographically different molecules are nearly parallel. The distances between the ring centers are 5.29 ± 0.02 Å and 6.06 ± 0.03 Å in structure 1 and 6.87 ± 0.02 Å, and 6.41 ± 0.03 Å in structure 2, between two tetrasubstituted and two trisubstituted rings, respectively, too high to allow significant interaction. Consequently, the apparent distortions, especially in the tetrasubstituted ring, are insufficient to explain the appreciable absorption at 238 nm.

Mechanistic Considerations. Dimer 2-2 is formed by combination of two radicals 2•. The unsymmetrical dimer 1-2 could be formed by combination of radicals 1• and 2•, but radical substitution of 1-Li by 2•, followed by hydrolysis of the formed lithium salt of 1-2 is also possible. The rearrangement of 1• to 2• is apparently faster than bimolecular combination of two 1• radicals to form 1-1, probably due to the high crowding in the transition state leading to 1-1. In spite of the higher stability of 3•, the reactions of 2• leading to 2-2 or 1-2 are faster than the unobserved 2• → 3• rearrangement.

The appreciable literature of reactions of 1-Li and 1-MgBr report no dimer formation. Likewise, dimers were not obtained by raising the temperature of a 1-Li solution from −78 °C to 20 °C in spite of reports of instability of the solution.[7b] Moreover, reaction of 1-Li with 1-Br did not give any dimer at 0 °C, 20 °C or 65 °C. Dimers were formed only in the presence of the carbonyl derivatives, which are apparently involved in the radical formation. The steric bulk of the organometallic reagent hinders the nucleophilic substitution and reduces its yield. However, a SET from the organometallic reagent to the carbonyl substrate, which may be the first step in a nucleophilic addition,[11] can take place due to its low sensitivity to steric effects. Combination of the two radicals will give the substitution products observed with 4 or 5. Radical 1• can also rearrange to 2•, which then gives dimers 1-2 and 2-2 (eq 3). The fate of the ArCOX radical is unknown.



(3)

The 1-2 to 2-2 ratios should primarily reflect the rate of 1• → 2• isomerization vs the selectivity in the combination of 2• with 2• and 1• if 1-2 is formed by radical combination. If 1-2 is formed by reaction of 2• with 1-Li, the ratio will be determined by the rates of this process and the dimerization rate of 2•. Destruction of the reagent by proton abstraction[7b] will give 1-H, which can react with 2• to form 1-2. The mechanism was not investigated further.

Experimental Section

Materials and Methods. 1-Br was prepared according to Pearson.[12] Product detection and analysis was by ^1H NMR and by HPLC using a Lichrosorb Si60 column and hexane eluent.

2,5-Bis(3,5-di-*tert*-butylphenyl)-2,5-dimethylhexane (2-2). (a) From 1-MgBr and Diphenylacetyl Chloride. To a stirred mixture of Mg turnings (0.3 g, 25 mM) in dry ether (10 mL) was added to a solution of 1-Br (2.28 g, 7 mM) and 1,2-dibromoethane (2.63 g, 14 mM) in dry ether (30 mL) dropwise during 30 min. Toluene (40 mL) was added, and stirring with gentle heating was continued until complete dissolution of Mg. A solution of diphenylacetyl chloride (1.13 g, 5 mM) in dry ether (10 mL) was

(10) Knauf, A. E.; Adams, R. *J. Am. Chem. Soc.* **1933**, *55*, 4704. Biali, S. E.; Kahr, B.; Okamoto, Y.; Aburatani, R.; Mislow, K. *Ibid.* **1988**, *110*, 1917.

(11) For example, (a) see: Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414 and references therein. (b) Ashby, E. C.; Bowers, J.; DePriest, R. *Tetrahedron Lett.* **1980**, *21*, 3541. (c) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59. (d) Holm, T. *Ibid.* **1990**, *44*, 279. (e) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

(12) Pearson, D. E.; Frazer, M. G.; Frazer, V. S.; Washburn, L. C. *Synthesis* **1976**, 621.

then added dropwise during 30 min, and the mixture was poured into an 0.1 M HCl solution (20 mL) and washed with 0.1 M aqueous K_2CO_3 solution and the organic phase was separated, dried ($MgSO_4$), and evaporated. Crystallization of the yellow solid from ethanol gave 0.7 g (41%) of **2-2**, mp 150 °C: UV λ_{max}(hexane) 220 nm (ϵ = 6000), 261 (600); IR ν_{max} (Nujol) 1600 (m, Ar) cm^{-1}; ^1H NMR δ ($CDCl_3$, room temperature) 1.23 (12 H, s, 4 Me), 1.31 (36 H, s, 4 *t*-Bu), 1.42 (4 H, s, 2 CH_2), 7.12 (4 H, d, Ar H), 7.21 (2 H, t, Ar H); ^{13}C NMR δ ($CDCl_3$, room temperature) 28.98 (Me), 31.60 (Me_3C), 34.93 (CMe_3), 37.65 (CH_2), 39.05 (C_2), 119.10 (C_p), 119.96 (C_o), 148.74 (C_{ipso}), 149.74 (C_m); mass spectrum (*m/z*, 70 eV, relative abundance, assignment) 490 (9, M), 246 (6, *t*-$Bu_3C_6H_3$), 231 (100, *t*-$Bu_2C_6H_3CMe_2$). Anal. Calcd for $C_{36}H_{58}$: C, 88.08; H, 11.79. Found: C, 88.06, H, 11.81.

(b) From 1-Li and Diethyl Oxalate. To a stirred solution of **1-Br** (3.75 g, 11.5 mM) in dry ether (100 mL) at 0 °C was added a solution of BuLi in hexane (1.05 equiv), and the mixture was stirred for 1.5 h at 0 °C in an argon atmosphere. Diethyl oxalate (0.75 mL, 5.5 mM) was added and the temperature was raised gradually overnight to 20 °C. Water (100 mL), followed by 10% AcOH (20 mL), was added. The organic phase was separated, washed with 5% $NaHCO_3$ solution (70 mL) and water, and dried ($MgSO_4$). The ether was evaporated, the residue dissolved in petroleum ether (30 mL), and the remaining solid was filtered, recrystallized (EtOH), and characterized as **2-2** (170 mg, 6%) by mp, IR, and ^1H NMR. **1-H** was also isolated.

1-(2,4,6-Tri-*tert*-butylphenyl)-2-(3,5-di-*tert*-butylphenyl)-2-methylpropane (1-2). From 1-Li and Oxalyl Chloride. To a stirred solution of **1-Br** (3.5 g, 1.08 mM) in freshly distilled THF (100 mL) at −78 °C under argon was added a solution of BuLi in hexane (1.1 equiv, 11.2 mM). After 2.5 h oxalyl chloride (0.5 mL, 5.8 mM) was added, stirring at −78 °C was continued for 18 h, and the solution was allowed to reach 0 °C. Water (120 mL) was added, the solvent was evaporated, and the residue was dissolved in EtOAc (150 mL), washed successively with water (100 mL), 5% aqueous $KHCO_3$ solution and water, dried ($MgSO_4$), and evaporated, leaving a greenish oil. Chromatography on silica using petroleum ether (60–80 °C) as eluent gave several fractions from which bis(2,4,6-tri-*tert*-butylphenyl) diketone (80 mg, 2.7%), mp 202–204 °C (lit.[9] mp 203–205 °C), **1-H** and 1,3,5-tri-*tert*-butylbenzoic acid, mp 277–9 °C (lit.[6b] mp 297 °C) (70 mg, 8.4%), and **1-2** (R_f 0.4) were obtained. Recrystallization (EtOH) yielded 250 mg (9.5%) of pure **1-2**, mp 82 °C: UV λ_{max} (hexane) 212 nm (42 700), 238 sh (9300); IR ν_{max} (Nujol) 1590 cm^{-1} (s, Ar); ^1H NMR δ ($CDCl_3$) 1.00 (6 H, s, 2 Me), 1.25 (18 H, s, 2-*o*-*t*-Bu tetrasubstituted ring), 1.29 (18 H, s, 2-*o*-*t*-Bu, trisubstituted ring), 1.31 (9 H, s, *p*-*t*-Bu, tetrasubstituted ring), 3.50 (2 H, s, CH_2), 6.99 (2 H, d, J = 1.8 Hz, *m*-Ar H, trisubstituted ring), 7.19 (2 H, s, *m*-Ar H, tetrasubstituted ring), 7.20 (1 H, t, J = 1.8 Hz, *p*-Ar H, trisubstituted ring); ^{13}C NMR δ ($CDCl_3$, room temperature, tentative assignment) 28.70 (Me), 31.52 (Me_3C), 31.56 (Me_3C), 34.38 (Me_3C), 34.90 (Me_3C), 38.44 (Me_3C), 41.00 (CH_2), 42.86 (C_2), 119.26, 120.80, 121.68 (C_o, C_p), 134.28 (C_m), 144.86 (C_m), 149.49 (C_{ipso}), 149.80 (C_{ipso}), 149.96 (C_{ipso}); mass spectrum (*m/z*, 70 eV, relative abundance, assignment) 259 (32, *t*-$Bu_3C_6H_2CH_2$), 231 (100, *t*-$Bu_2C_6H_3CMe_2$); (chemical ionization, CH_5^+; *m/z*, relative abundance, assignment) 489 (7, M − 1), 475 (19, M − Me), 379 (33, MH − $2C_4H_8$), 259 (78, *t*-$Bu_3C_6H_2CH_2$), 245 (100, *t*-$Bu_3C_6H_3$), 231 (70, *t*-$Bu_2C_6H_3CMe_2$), 219 (13, 245 − C_2H_2), 189 (42, *t*-$Bu_2C_6H_3$). Anal. Calcd for $C_{36}H_{58}$: C, 88.06; H, 11.81. Found: C, 88.34; H, 11.79.

Reaction of 1-Li with Methyl Chloroglyoxylate. A solution of **1-Br** in dry THF (7.4 g, 22.8 mM) at −10 °C under argon, to which a solution of BuLi (1.05 equiv) was added, was stirred for 1 h. Methyl chloroglyoxylate (0.7 mL, 7.6 mM) was added and the temperature increased gradually to room temperature. A mixture of several compounds (by NMR) was precipitated. After being washed with water (20 mL), the solvent was evaporated. When the residue was dissolved in MeOH, a second precipitate was formed. Recrystallization ($CHCl_3$) yielded 170 mg (1.5%) of **2-2**. Evaporation of the filtrate to dryness and redissolution in MeOH gave **1-2** as a white precipitate (110 mg, 1%), which was characterized by NMR, IR, mp, and X-ray crystal diffraction. Methyl (2,4,6-tri-*tert*-butylphenyl)glyoxylate and **1-H** were also isolated.

X-ray crystal structure analysis of 1-2: space group $P1$, a = 16.030 (6) Å, b = 19.743 (7) Å, c = 10.659 (3) Å, α = 95.51 (3)°, β = 94.85 (3)°, γ = 90.79 (4)°, V = 3345 (1) Å^3, Z = 4, ρ_{calcd} = 0.98 g cm^{-3}, μ(Mo K_α) = 0.26 cm^{-1}, number of unique reflections 8756, number of reflections with $I > 3\sigma_I$ 4799, R = 0.090.

Collection of data and analysis was as reported previously.[13]

Acknowledgment. We are indebted to Dr. Shmuel Cohen for X-ray diffraction. This work was supported by the Commission for Basic Research, the Israel Academy for Sciences and Humanities, to whom we are grateful.

Supplementary Material Available: Tables giving bond lengths (Table S1), bond angles (Table S2), and positional (Table S4) and thermal parameters (Table S5) and Figures S1–S3 giving the unit cell and the stereoscopic views of **1-2** (14 pages); observed and calculated structure factors for **1-2** (Table S3) (29 pages). Ordering information is given on any current masthead page.

(13) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.

Facile and Selective Epoxidation with the H_2O_2/Vilsmeier Reagent System

Jean Rodriguez* and Jean-Pierre Dulcère

Laboratoire de Synthèse Organique, SM³B URA CNRS 1411, Université d'Aix-Marseille III, Faculté des Sciences de St Jérôme, D12 Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 13, France

Received February 6, 1990

Direct epoxidation of an alkene is typically accomplished by using the combination of an organic peroxide and a metal catalyst[1] or by an organic peracid.[2] *m*-Chloroperbenzoic acid (MCPBA)[3] is one of the most commonly used oxidants in this field. Utilization of hydrogen peroxide as primary oxidant[4] has received much attention, but because of its low electrophilicity it requires, for nonconjugated carbon–carbon double bonds, activation either by coordination to a metal[5] or by addition to a polarized multiple bond. Peroxycarboximidic acid formed in situ by addition of H_2O_2 to a nitrile[6] is one of the most useful applications of this O–O bond activation.

More recently it has been shown that a trichloromethyl substituent enhances the reactivity of the nitrile.[7] Peroxycarboximidic acids exhibit almost the same reactivity, but are less chemoselective reagents, than MCPBA or magnesium monoperphthalate (MMPP)[8] toward polyolefins.[9] *N*-Arylperoxycarbonic acids,[10] peroxy-

(1) (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63. (b) Pfenninger, A. *Synthesis* **1986**, 89.

(2) (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 292. (b) Swern, D. *Org. React.* **1953**, *7*, 378. (c) Swern, D. *Organic Peroxides*; Wiley Interscience: New York, 1971; Vol. II, p 355.

(3) Fieser, M.; Fieser, L. F. *Reagents for Organic Synthesis*; Wiley Interscience: New York, 1967; Vol. 1, p 135.

(4) For a review, see: Rebek, J. *Heterocycles* **1981**, *15*, 517.

(5) (a) Sheldon, R. A.; Kochi, J. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; p 275. (b) Sheldon, R. A. "Metal Catalyzed Epoxidation of Olefins with Hydrogen Peroxides" in *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, 1981; p 3.

(6) (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1953**, *75*, 3961. (b) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* **1961**, *26*, 659. (c) Payne, G. B. *Tetrahedron* **1962**, *18*, 763.

(7) Arias, L. A.; Adkins, S.; Nagel, C. J.; Bach, R. D. *J. Org. Chem.* **1983**, *48*, 888.

(8) Brougham, P.; Cooper, M. S.; Cummerson, D. A.; Heaney, H.; Thompson, N. *Synthesis* **1987**, 1015.

0022-3263/91/1956-0469$02.50/0