Table II. Selected Torsion Angles[a] in 1,1,1,3,3,3-Hexaphenylpropane and Related Compounds

torsion angle	Tt_2CH_2,[b] X = C(1)	Tp_2CH_2,[c] X = C(1)	Tt_2O,[d] X = O	Tt_2S,[e] X = S
C(40)-X-C(10)-C(11)	65.0	10.8	−2.8	−46.4
C(40)-X-C(10)-C(21)	−62.7	−114.3	121.4	83.9
C(40)-X-C(10)-C(31)	179.9	133.1	−127.0	−164.1
C(10)-X-C(40)-C(41)	68.5	54.3	78.0	78.2
C(10)-X-C(40)-C(51)	−61.6	−75.3	−53.8	−48.5
C(10)-X-C(40)-C(61)	−178.6	171.7	−171.8	−165.8
X-C(10)-C(11)-C(12)	43.6	−2.5	−76.9	128.6
X-C(10)-C(11)-C(16)	−144.1	−178.9	102.2	−50.1
X-C(10)-C(21)-C(22)	−91.5	2.4	1.2	168.5
X-C(10)-C(21)-C(26)	83.6	−170.2	177.6	−6.7
X-C(10)-C(31)-C(32)	−1.6	−2.0	−33.1	127.2
X-C(10)-C(31)-C(36)	178.5	172.5	151.5	−55.5
X-C(40)-C(41)-C(42)	32.8	−1.8	16.6	−141.8
X-C(40)-C(41)-C(46)	−155.3	176.7	−171.2	42.6
X-C(40)-C(51)-C(52)	−76.8	4.7	−61.0	−123.6
X-C(40)-C(51)-C(56)	99.2	−172.5	121.2	62.5
X-C(40)-C(61)-C(62)	−14.7	−3.8	147.2	−124.2
X-C(40)-C(61)-C(66)	168.2	177.5	−39.6	58.2

[a] In degrees. [b] Present work. [c] Calculated from atomic parameters in ref 1f (Table II, unprimed molecule). [d] Reference 2, with atoms renumbered. Torsion angles calculated by the Cambridge crystallographic database program GEOM78. [e] Torsion angles calculated from the atomic coordinates in ref 3 (Table 2; atoms renumbered).

Tt_2X have a similar effect in the widening of the central C–X–C bond angle,[8] it has also brought to light a striking difference in the effect of these groups on molecular conformation.[9]

Experimental Section

A solution of triphenylmethyl chloride (1.0 g) in 20 mL of anhydrous benzene was stirred with activated zinc powder (1.5 g) for 5 days at room temperature under an inert atmosphere. The suspension was filtered and a solution of diazomethane in alcohol–ether was slowly added until the color characteristic of the trityl radical had disappeared. The reaction mixture was stirred for an additional 8 h and quenched with acetic acid. The solvent was evaporated and the residual white solid recrystallized from acetic acid and then from heptane. The product (0.41 g, 46%) had the following properties: mp 214–216 °C (lit.[4a] mp 216 °C); ^1H NMR (89.5 MHz, $C^2H_2Cl_2$) δ 4.25 (s, 2 H), 7.00 (m, 30 H); $^{13}C\{^1H\}$ NMR (22.5 MHz, $C^2H_2Cl_2$) δ 48.92, 125.63, 127.58, 129.86, 147.57; $^1J_{CH}$ (central CH_2) = 126.9 Hz.

The crystals were triclinic, space group $P\bar{1}$, with $a = 9.267$ (3), $b = 10.654$ (4), $c = 15.976$ (5) Å, $\alpha = 88.13(2)$, $\beta = 74.53$ (2), $\gamma = 67.31$ (2)°, and $d_{calcd} = 1.189$ g cm^{-3} for $Z = 2$ ($C_{39}H_{32}$, $M_r = 500.68$). The intensity data were measured on a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.25 × 0.25 mm. A total of 3758 independent reflections were measured for $\theta < 57°$, of which 3125 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[10] and was refined by full-matrix least squares. Eight reflections that were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.040$ and $wR = 0.044$ for the remaining 3117 observed reflections. The final difference map has no peaks greater than ±0.2 e A^{-3}.

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Registry No. Tt_2CH_2, 82891-67-6; triphenylmethyl chloride, 76-83-5; diazomethane, 334-88-3; trityl radical, 2216-49-1.

Supplementary Material Available: Final atomic parameters for hydrogen atoms, final anisotropic thermal parameters, bond lengths, bond angles, with standard deviations (Tables III–VI) (4 pages). Ordering information is given on any current masthead page.

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[8] It therefore becomes safe to predict that the C–O–C angle in Tp_2O [Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547] assumes a value close to that found[2] for Tt_2O.

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Attempted Spin Trapping of *tert*-Butylperoxyl Radical by Trifluoronitrosomethane[1]

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Although there appears to be rather general agreement that peroxyl radicals, ROO·, can be spin trapped by certain nitrones,[3-9] there is no such agreement regarding their trapping by nitroso compounds. The most popular nitroso spin trap, 2-methyl-2-nitrosopropane (MNP), has been reported to give peroxyl radical spin adducts, $Me_3CN(\dot{O})OOR$.[8] It has also been reported to give only the spin adducts of the corresponding alkoxyl radical, $Me_3CN(\dot{O})OR$.[10] It occurred to us that trifluoronitrosomethane

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might prove to be a more definitive and satisfactory nitroso spin trap for peroxyl radicals than MNP because the electron-withdrawing CF_3 group would be expected to stabilize the spin adduct, $CF_3N(\dot{O})OOR$.[11]

Photolysis of an oxygen-saturated solution of di-*tert*-butyl ketone in $CFCl_3$ at 173 K in the cavity of an EPR spectrometer yielded the persistent *tert*-butylperoxyl radical (single line, $g = 2.0146$). On cutting off the UV irradiation and, in the dark,[14] passing a fine stream of bubbles of CF_3NO through the solution, the *tert*-butylperoxyl radical was immediately destroyed with the formation of another persistent radical. The EPR parameters for this second radical, viz.,[16] $g = 2.0059$, $a^N(1N) = 22.76$ G, $a^F(3F) = 5.80$ G, identify it as a nitroxide. Repetition of this experiment using isotopically labeled oxygen (74 atom % ^{17}O) caused the doubly labeled *tert*-butylperoxyl radical ($a^{17}O = 23.4$ and 17.6 G)[18,19] to be converted to nitroxide, which showed additional hyperfine splitting by only a single ^{17}O atom ($a^{17}O = 0.93$ G)[16] and no line broadening that might be attributable to a second ^{17}O atom. This suggests that the observed nitroxide is not the peroxyl adduct, **1**, but is instead the *tert*-butoxyl adduct, **2**, formed by the reaction sequence:

$$(Me_3C)_2C{=}O \xrightarrow{h\nu} 2Me_3C\cdot + CO$$

$$Me_3C\cdot + O_2 \rightarrow Me_3COO\cdot$$

$$Me_3COO\cdot + CF_3NO \rightarrow \underset{\mathbf{1}}{CF_3N(\dot{O})OOCMe_3}$$

$$CF_3N(\dot{O})OOCMe_3 \rightarrow CF_3NO_2 + Me_3CO\cdot$$

$$Me_3CO\cdot + CF_3NO \rightarrow \underset{\mathbf{2}}{CF_3N(\dot{O})OCMe_3}$$

Further confirmation of this spectral assignment was obtained by generating *tert*-butoxyls by the thermal decomposition of di-*tert*-butyl hyponitrite in the presence of $CF_3NO\cdot$ in C_6F_6 at 300 K. A nitroxide having the EPR parameters reported above, which in this case *must* be **2**, was obtained.

$$Me_3CON{=}NOCMe_3 \rightarrow 2Me_3CO\cdot + N_2$$

Final confirmation that CF_3NO does not yield an observable peroxyl spin adduct was obtained by generating *tert*-butoxyl and *tert*-butylperoxyl radicals simultaneously in its presence. A solution of di-*tert*-butyl trioxide[13] was prepared by UV photolysis of di-*tert*-butyl peroxide and isobutane in oxygen-saturated $CFCl_3$ at 163 K. The light was cut off[14] and CF_3NO was bubbled into the solution; the temperature was then allowed to increase to ca. 240 K at which point the trioxide decomposes[13] to form the alkoxyl and peroxyl radicals. Only nitroxide **2** was observable.

$$Me_3COOOCMe_3 \rightarrow Me_3CO\cdot + Me_3COO\cdot$$

Since CF_3NO does not yield an observable *tert*-butylperoxyl spin adduct, it is highly improbable that MNP could do so. Our results therefore support the conclusion[10] that the reaction of MNP with peroxyl radicals yields the alkoxyl spin adduct. The contrary conclusion[8] rests on an experiment in which $Me_3CO^{17}O^{17}OCHMe_2$ (generated by photolysis of $Me_3COOCMe_3$ in $^{34}O_2$-saturated propane) was allowed to warm up to 263 K in the presence of MNP. Two ^{17}O-labeled nitroxides were detected. Their EPR parameters were $g = 2.0057$, $a^N = 27.25$ G, $a^{^{17}O}(1\,^{17}O) = 1.03$ G, and $g = 2.0056$, $a^N = 28.7$ G, $a^{^{17}O}(1\,^{17}O) = 4.6$ G. In a separate experiment the former radical was identified as $Me_3CN(\dot{O})^{17}OCMe_3$. The latter radical was assigned as a peroxyl spin adduct, $Me_3CN(\dot{O})^{17}OOR$, with R = Me_3C or Me_2CH. We suggest that the latter radical was actually the isopropoxyl spin adduct, $Me_3CN(\dot{O})^{17}OCHMe_2$. This suggestion receives support from the fact that for $Me_3CN(\dot{O})OR$ radicals the value of a^N decreases along the series R = Me, Et, *i*-Pr, *t*-Bu.[20–22] In 2-propanol as solvent, $a^N = 29.0$ G for R = *i*-Pr[21] and 27.06 G for R = *t*-Bu,[22] values which are in satisfactory agreement with $a^N = 28.7$ G for R = *i*-Pr (our assignment) and 27.25 G for R = *t*-Bu (original[8] assignment). Such a comparatively large change in a^N for what would appear to be a minor change in the nature of R implies a significant difference in the configuration and/or conformation of the two radicals. Such a change in geometry could, we suggest, also be sufficient to change $a^{^{17}O}$ from 1.0 G for R = *t*-Bu to 4.6 G for R = *i*-Pr.

Finally, we note that although our hope that CF_3NO would yield observable spin adducts with peroxyl radicals was not realized, it did yield a spin adduct with *tert*-butoxyl that was very much more persistent than the MNP–*tert*-butoxyl spin adduct[23] and other alkoxy alkyl nitroxides. Thus, for example, $CF_3N(\dot{O})OCMe_3$ at an initial concentration of ca. 1.1×10^{-5} M in $CFCl_3$ decayed with first-order kinetics and with a half-life of ca. 105 s at 313 K.[24] For comparison, the half-life of $Me_3CN(\dot{O})OCMe_3$ in di-*tert*-butyl peroxide as solvent was found[23] to be ca. 5 s at the same temperature. Trifluoronitrosomethane may therefore have some advantages over MNP as a spin trap for alkoxyl radicals.

Registry No. $Me_3COO\cdot$, 3395-62-8; CF_3NO, 334-99-6; $CF_3N(O\cdot)OCMe_3$, 82880-42-0.

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An Unusual Dimer Resulting from the Addition of Ethyl Chloroformate to a 2-Lithio-1,3-dithiane

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Some years ago, Corey and Seebach[1] reported that treatment of 2-lithio-1,3-dithianes **1** at −70 °C with a large

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