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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[10] Pfab, J. *Tetrahedron Lett.* **1978**, 843–846.

[11] In this connection note that CF_3OOOCF_3[12] is thermally much more stable than $Me_3COOOCMe_3$.[13]

[12] Anderson, L. R.; Fox, W. B. *J. Am. Chem. Soc.* **1967**, *89*, 4313–4315. Thompson, P. G. *Ibid.* **1967**, *89*, 4316–4319.

[13] Bartlett, P. D.; Günther, P. *J. Am. Chem. Soc.* **1966**, *88*, 3288–3294. Bartlett, P. D.; Lahav, M. *Isr. J. Chem.* **1972**, *10*, 101–109.

[14] The photolysis of CF_3NO with either UV or visible light yields the extremely persistent $(CF_3)_2NO\cdot$ radical.[15]

[15] Chatgilialoglu, C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 4833–4837.

[16] The EPR spectrum of this radical shows some interesting changes with temperature that will be reported in detail elsewhere.[17]

[17] Chatgilialoglu, C.; Ingold, K. U. *J. Phys. Chem.*, in press.

[18] Adamic, K.; Ingold, K. U.; Morton, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 922–923.

[19] Howard, J. A. *Can. J. Chem.* **1972**, *50*, 1981–1983.

[20] Sargent, F. P.; Gardy, E. M. *J. Phys. Chem.* **1976**, *80*, 854–856.

[21] Sargent, F. P.; Gardy, E. M. *J. Phys. Chem.* **1977**, *81*, 1215–1216.

[22] Janzen, E. G.; Coulter, G. A. *Tetrahedron Lett.* **1981**, *22*, 615–619.

[23] Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 297–304.

[24] The final products can be presumed to be *N,N′*-di-*tert*-butoxyl-*N,N′*-bis(trifluoromethyl)hydrazine and trifluoronitromethane.[25]

[25] Barton, D. H. R.; Harris, R. L.; Hesse, R. H.; Pechet, M. M.; Urban, F. J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2344–2346.

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

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Received April 27, 1982

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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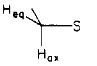
[1] E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1077 (1965).

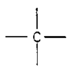
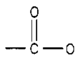
0022-3263/82/1947-4362$01.25/0

Table I. ^{1}H NMR Data for 5

hydrogen	chemical shift[a] (multiplicity)	coupling constant, Hz
$CH_3COC{=}O$	1.28 (t)[b]	7.0
$SCH_2CH_2CH_2S$	1.84 (quint)	7.0
$CH_2CH_2C{=}C(2)$	2.0-2.2 (m)	
$CH_2C{=}C(1)$	2.0-2.2 (m)	
$CH_2C{=}C(1)$	2.4 (m)	
$SCH_2CH_2CH_2S$	2.60 (t)	7.0
	2.70 (t)	7.0
	H_{ax} 3.29 (d, d, d)	J_{gem} = 14.0,
	H_{eq} 2.6-2.7 (m)	J_{vic} = 12.0, 2.0
$CH_2OC{=}O$	4.26 (q)	7.0
$CH_2{=}C$	4.99 (d, d)	J_{cis} = 10.0,
		J_{gem} = 2.0
	5.06 (d, d)	J_{trans} = 18.0
$CH_2CH{=}CH_2$	5.83 (d, d, t)	J_{vic} = 7.0

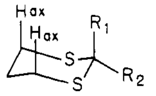
[a] Chemical shifts in parts per million relative to internal tetramethylsilane. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Table II. ^{13}C NMR Data for 5

carbon	chemical shift[a] (multiplicity)
CH_3CO	14.04 (q)[b]
$SCH_2CH_2CH_2S$	25.00 (t)
$SCH_2CH_2CH_2S$	27.43 (t)
$SCH_2CH_2CH_2S$	28.51 (t)
$-S_3CH_2CH_2C{=}C$	42.09 (t)
$SCH_2CH_2C{=}C$	32.86 (t)
$CH_2C{=}C$	31.92 (t)
	28.92 (t)
$SCH_2CH_2CH_2S$	28.33 (t)
OCH_2	62.03 (t)
	61.15 (s)
	62.25 (s)
$CH_2{=}C$	115.20 (t)
	115.35
$CH{=}C$	137.00 (d)
	137.38
	168.62 (s)

[a] Chemical shifts in parts per million relative to internal tetramethylsilane. [b] s = singlet, d = doublet, t = triplet, q = quartet.

excess of ethyl chloroformate provided the ethyl carboxylates **3** in good yields. As a method for the preparation of various α-keto esters, we required a synthesis of dithiane ester **4**. Under somewhat different conditions, addition of ethyl chloroformate[2] to a −50 °C tetrahydrofuran solution of 2-(buten-1-yl)-2-lithio-1,3-dithiane (**2**) afforded not only the desired product **4** in low yield but a second, more polar dimeric compound. We report in this paper the structural assignment **5** for this anomalous compound.



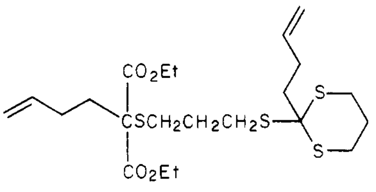
1, $R_1 = CH_3, CH_2Ph; R_2 = Li$
2, $R_1 = CH_2{=}CHCH_2CH_2; R_2 = Li$
3, $R_1 = CH_3, CH_2Ph; R_2 = CO_2C_2H_5$
4, $R_1 = CH_2{=}CHCH_2CH_2; R_2 = CO_2C_2H_5$

From a cursory examination, the ^{1}H NMR spectra of both compounds appeared very similar. The only distinguishing features in their spectra was found in the ^{1}H integration. The spectrum of **4** showed, as expected, a 1:1 ratio for the two downfield dithiane ring hydrogens[3] (H_{ax}, δ 3.29) relative to the carbethoxy hydrogens ($CO_2CH_2CH_3$). In the spectrum of the unknown, integration revealed two equivalent carbethoxy groups for each dithiane ring ($CO_2CH_2CH_3$; H_{ax}, ratio 2:1).

To determine all the possible structures for the dimer that best satisfy the NMR requirements, the NMR data was input to a computer-assisted structure-elucidation program (CASE).[4] The observed ^{1}H and ^{13}C spectral properties of the unknown product are presented in Tables I and II.

There was no duplication in the ^{1}H absorptions for the carbethoxy and butenyl moieties. Consequently, these groups resided in a symmetrical or nearly symmetrical magnetic environment with respect to each other. The ^{13}C spectrum further reflected the symmetry properties of the molecule, e.g., the vinyl carbons were only slightly displaced, a single set of signals for the carbethoxy groups, and doubly intense lines corresponding to the carbons adjacent to the sulfurs ($SCH_2CH_2CH_2S$ and $SCH_2CH_2CH_2SCH_2$. The most revealing structural information obtained from the ^{13}C spectrum was the presence of two quaternary carbons at 61.15 and 62.25 ppm.

Among the possible structures generated by CASE, only **5**, **6**, and **7** were in agreement with the observed NMR data.



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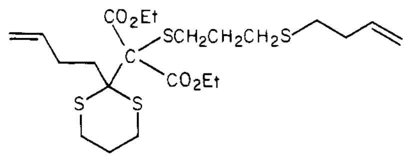

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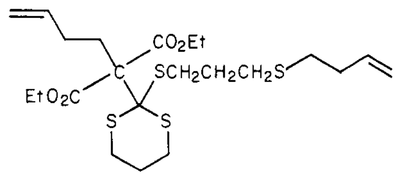

7

Structures **6** and **7** can be ruled out by considering their feasibility of formation. The assignment of structure **5** to the dimer was also consistent with the experimental findings and mechanism of formation. The yield of **5** varied somewhat, depending on the rate of ethyl chloroformate addition and reaction temperature. Addition of ethyl chloroformate to a −15 °C solution of **2**[5] or a slow addition of reagent favored the formation of **5**. Irrespective of the addition rate and temperature, TLC analysis of the

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[2] Although the large excess of ethyl chloroformate used in ref 1 was not specified, we suspect these workers employed greater than 2 equiv. The results reported herein were obtained with less than 2 equiv of reagent.

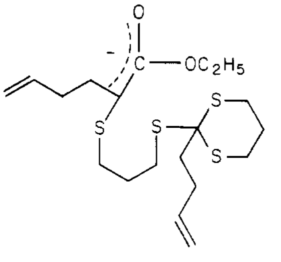
[3] For a discussion of the ^{1}H NMR properties of 1,3-dithianes, see E. L. Eliel, A. A. Hartman, and A. G. Abatjoglon, *J. Am. Chem. Soc.*, **96**, 1807 (1974).

[4] (a) L. A. Dolak and M. E. Monk, Current Chemotherapy and Infectious Disease Proceedings of the 11th ICC and 19th ICAAC American Society of Microbiology, 1980, p 467–469; (b) L. A. Dolak and C. DeBoer, *J. Antibiot.*, **33**, 83 (1980), and references cited therein.

[5] Even when the reaction was carried out by rapid addition of excess ethyl chloroformate (10 equiv) to a −73 °C tetrahydrofuran solution of **2** (1 equiv), the formation of **5** was not totally suppressed. TLC analysis indicated 10–15% of dimer **5** and 85–90% of **4**.

crude reaction mixture always indicated **5** as the major side product. However, when an inverse addition procedure was used, **4** was then obtained as the only product in excellent yield (85%).[6]

A plausible mechanism to account for the formation of **5** involves reaction at sulfur of dithiane **4** with the lithio anion **2** to generate the ester enolate **8**. In the presence



8

of ethyl chloroformate, **8** was trapped to yield dimer **5**. It was surprising that **2** served as a nucleophile toward sulfur and not the carbonyl group of **4**.[7]

Further experiments are required to determine the generality of this unusual dimerization reaction. We suspect, however, that formation of dimeric side products, such as **5**, can occur whenever 2-lithio-1,3-dithiane derivatives are alkylated with ethyl chloroformate. The inverse addition procedure allows the reaction to proceed in the normal manner. This technique insures a high yield of the desired product and avoids the use of excessive amounts of ethyl chloroformate.

Experimental Section

All ^1H NMR spectra were run in $CDCl_3$ solutions with tetramethylsilane as the internal standard, using either a Varian A-60A or a Varian XL-200 spectrometer operating in the FT mode. All ^{13}C NMR spectra were run on the same Varian XL-200 tuned to the carbon resonance frequency (50.3 MHz). The decoupler was gated on and off during various experiments to obtain noise-decoupled, off-resonance and coupled with NOE enhancement spectra. High-resolution mass spectra were recorded with a CEC 21-110B spectrometer at 70 eV.

Typical Procedure for the Addition of Ethyl Chloroformate to 2-(Buten-1-yl)-2-lithio-1,3-dithiane (2). To a magnetically stirred solution of 2-(buten-1-yl)-1,3-dithiane (11.30 g, 64.94 mmol) in 200 mL of tetrahydrofuran, cooled in a −35 °C bath, was added 41.40 mL of *n*-butyllithium (1.6 M in hexane, 66.24 mmol). Stirring was continued for 1.5 h while the cooling bath temperature was maintained between −25 and −20 °C. At the end of this period, the resulting rust-colored solution of **2** was cooled to −50 °C, and 9.82 g (90.92 mmol) of ethyl chloroformate was added over a 3–5-min period. After addition, the cooling bath was removed and the reaction allowed to warm to 0 °C. The solution was then poured into 150 mL of cold 1 N potassium hydrogen sulfate solution and thoroughly extracted with ether. The combined ether extracts were successively washed with 1 N sodium hydroxide solution, water, and saturated brine and dried through anhydrous sodium sulfate. Removal of the solvent in vacuo gave a residual yellow oil, which was chromatographed with 1 kg of silica gel. Elution with Skellysolve B-ethyl acetate (15:1, v/v) afforded 4.05 g of **4** and 5.20 g of dimer **5**, both as viscous colorless oils [TLC, Skellysolve-B–ethyl acetate (9:1)]: R_f 0.36 for **5** and 0.46 for **4**; mass spectrum, *m/e* calcd for **4** ($C_{11}H_{18}O_2S_2$, M^+) 246.0748, found 246.0735; mass spectrum, *m/e* for **5** calcd for $C_{14}H_{23}O_4S_2$ ($M^+ - \overline{SCH_2CH_2CH_2S(CH_2CH_2CH{=}CH_2)C}H$) 319.1038, found 319.1043.

Anal. Calcd for **4** ($C_{11}H_{18}O_2S_2$): C, 53.62; H, 7.36. Found: C, 53.87; H, 7.52. Calcd for **5** ($C_{22}H_{36}O_4S_4$): C, 53.62; H, 7.36. Found: C, 53.85; H, 7.42.

In other experiments, we have observed by TLC an increase in yield of **5** with respect to **4** when either the ethyl chloroformate addition was extended over a 15-min period or added to a −15 to −10 °C solution of **2**.

Inverse Addition Procedure. **2** was prepared as described above from 4.55 g (26.15 mmol) of 2-(buten-1-yl)-1,3-dithiane and 16.70 mL (26.70 mmol) of 1.6 M *n*-butyllithium in 100 mL of tetrahydrofuran. The solution of **2** was then added via a double needle canula, using nitrogen pressure over a 15-min period to a −78 °C solution of ethyl chloroformate (4.24 g, 39.22 mmol) in 30 mL of tetrahydrofuran. The resulting solution was allowed to warm to 0 °C and worked up in the same manner as previously described to yield 5.02 g (85%) of **4**.

Registry No. 4, 82951-41-5; 5, 82963-09-5; 2-(3-buten-1-yl)-1,3-dithiane, 16885-20-4; ethyl chloroformate, 541-41-3.

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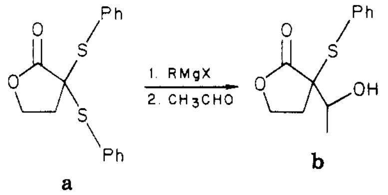
[6] D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975). These authors obtained by inverse addition a 60% yield of **3** (R = CH_3) when 10 mmol of **1** (R = CH_3) was added to a −73 °C tetrahydrofuran solution of 200 mmol of ethyl chloroformate.

[7] B. M. Trost and M. T. K. Mao, *Tetrahedron Lett.*, 3523 (1980). A similar reaction was observed where a Grignard reagent reacted with lactone a exclusively at sulfur and the resulting enolate trapped with acetaldehyde to give alcohol b.



a b

Synthesis of 7*H*- and 9*H*-Cyclopenta[*a*]pyrene

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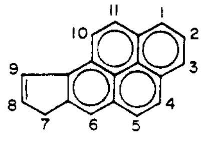
Received March 23, 1982

The polycyclic hydrocarbons 7*H*- and 9*H*-cyclopenta[*a*]pyrene (**1** and **2**), unknown prior to these studies, are



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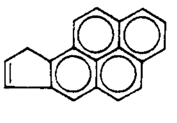

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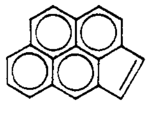

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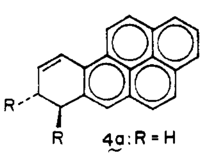
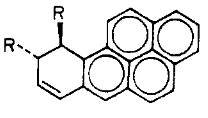


4a: R = H
b: R = OH



5a: R = H
b: R = OH

of interest as potential mutagens and carcinogens to test theories of carcinogenesis. The 7*H* isomer, **1**, is structurally related to cyclopenta[*cd*]pyrene (**3**), 7,8-dihydrobenzo[*a*]pyrene (**4a**), and *trans*-7,8-dihydroxy-7,8-dihydrobenzo[*a*]pyrene (**4b**) in that these molecules all contain an olefinic bond linked to the 1-position of pyrene. The latter three compounds exhibit mutagenic[1-4] and carcinogenic[3-5]

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[1] Eisenstadt, E.; Gold, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1667.

0022-3263/82/1947-4364$01.25/0