examined previously is $(Me_3Si)_3C\cdot$ which has a half-life of only 2 hr at this temperature[3,6]

(D) The $t$-Bu$(Me_3Si)\dot{C}CH(SiMe_3)_2$ radical, **2**, was prepared by photolysis of $t$-BuC$\equiv$CH, $Me_3SiH$, and $t$-BuOO-$t$-Bu (1:2:4 v/v). At 50° the half-life of 3 × $10^{-6}$ $M$ **2** was 23 hr. Storage of a much more concentrated solution of **2** for many hours at 50° left a residue of **1** (about 3% based on the initial **2**).

$$Me_3Si\cdot + t\text{-BuC}\equiv CH \xrightarrow{\sim 97\%} t\text{-Bu}\dot{C}=CHSiMe_3 \xrightarrow{2Me_3Si\cdot} 2$$

$$\xrightarrow{\sim 3\%} Me_3Si(t\text{-Bu})C=\dot{C}H \longrightarrow$$

$$t\text{-Bu}\cdot + Me_3SiC\equiv CH \xrightarrow{3Me_3Si\cdot} 1$$

The $(t$-Bu$)_2\dot{C}CH(SiMe_3)_2$ radical, **3**, was generated by $Me_3Si\cdot$ addition to $(t$-Bu$)_2C=CH_2$ *via* the intermediate $(t$-Bu$)_2\dot{C}CH_2SiMe_3$ radical[2] and by $Me_3Si\cdot$ addition to $(t$-Bu$)_2C=CH$-$t$-Bu (presumably *via* the $(t$-Bu$)_2\dot{C}CH$-$(t$-Bu$)SiMe_3$ radical which was too short lived to be positively identified). The latter method of preparation gave **3** which, at concentrations in the range 2 × $10^{-4}$ to 2 × $10^{-5}$ $M$, decayed with first-order kinetics and had a half-life of 2.3 hr at 50°.

$$Me_3Si\cdot + (t\text{-Bu})_2C=CH_2 \longrightarrow (t\text{-Bu})_2\dot{C}CH_2SiMe_3$$

$$\searrow t\text{-BuO}\cdot$$

$$(t\text{-Bu})_2C=CHSiMe_3 \xrightarrow{Me_3Si\cdot} 3$$

$$\nearrow -(t\text{-Bu}\cdot)$$

$$Me_3Si\cdot + (t\text{-Bu})_2C=CHt\text{-Bu} \longrightarrow (t\text{-Bu})_2\dot{C}CH(t\text{-Bu})SiMe_3$$

The $(t$-Bu$)_2\dot{C}CH(t$-Bu$)_2$ radical, **4**, was prepared by hydrogen abstraction by $t$-BuO$\cdot$ from the parent hydrocarbon.[3] This radical also decays with first-order kinetics, $\tau_{1/2}$ = 9.8 sec at 25°.

The stability of the foreging radicals decreases from **1** to **4**. Radicals **1**, **2**, and **3** probably decay by $\dot{C}H_3$ elimination from an $\alpha$-substituent, such a process occurring more readily from $t$-Bu than from $Me_3Si$. Radical **4** probably loses a $\beta$-$(t$-Bu$\cdot)$. Unless **1** decays by a bimolecular process at high concentrations (*i.e.*, a disproportionation), we see no reason why it should not be isolated if a more convenient source is discovered.

The epr parameters of **1**, **2**, **3**, and **4** are listed in Table I. Values of $a^{H\beta}$ are so low that they are within the line width for **2**, **3**, and **4**. That is, proton splittings are not completely resolved in these radicals and so they all yield a *single line epr spectrum* that is flanked *only* by the appropriate $^{13}C$ and/or $^{29}Si$ satellites. Only for radical **1** are the protons on the $\alpha$-substituents fully resolved (see Figure 1). The principal multiplet of **1** can be reproduced extremely well by computer simulation using at least four combinations of proton coupling constants, a line width $(\Delta H_{pp})$ = 0.1 G, and $a^{13C}$ $(6 ^{13}C)$ = 4.88 G, *viz:* (i) $a^H$ (9 H) = 0.135, $a^H$ (9 H) = 0.27, $a^H$ (1 H) = 0.675 G; (ii) $a^H$ (9 H) = 0.135, $a^H$ (9 H) = 0.405 G; (iii) $a^H$ (10 H) = 0.135, $a^H$ (9 H) = 0.405 G; (iv) $a^H$ (9 H) = 0.135, $a^H$ (1 H) = 0.27, $a^H$ (9 H) = 0.405 G. The hyperfine coupling to the lone $\beta$-H must therefore be uniquely small,[7] and in fact pos-

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(7) The lowest $a^{H\beta}$ for a tetrasubstituted ethyl in solution known to us is 3.68 G for 9,9′-bifluorenyl-9-yl.[8] The exceptionally low value of $a^{H\beta}$ in **1** may, in part, be a consequence of the known ability of $\alpha$-silicon substituents to "mop-up" a good deal of electron density.[9]

(8) F. A. Neugebauer and R. W. Groh, *Tetrahedron Lett.*, 1005 (1973).

sibility (i) was eliminated by treating $(CD_3)_3Si\cdot$ with $CH_3CN$. The resulting $[(CD_3)_3Si]_2\dot{C}CH[Si(CD_3)_3]_2$ radical had no resolvable deuteron couplings and the width $(\Delta H_{pp})$ of the principal line was only 0.48 G. The $\beta$-H coupling in **1** must therefore be $\leq 0.27$ G.

In substituted ethyl radicals, values of $a^{H\beta}$ can be approximately described by the empirical relation,[2,10] $a^{H\beta}$ = $A$ + $B$ $\cos^2\theta$, where $\theta$ is the angle between $C_\alpha 2p_z$ axis and the $C_\alpha$, $C_\beta$, $H_\beta$ plane. For the constants, $A$ and $B$ values of 0–5 and 40–45 G have been suggested.[10] The very small value of $a^{H\beta}$ for **1** (and also for **2**, **3**, and **4**) implies that $\theta$ = 90° (*i.e.*, $a^{H\beta}$ = $A$).



These radicals must be locked into this conformation by steric factors.[11,12] The relatively large values of $a^{29Si}\gamma$ also support this conformational assignment.[11] Moreover, since $R_\alpha$ and $R'_\alpha$ are always magnetically inequivalent, our general failure to resolve splittings due to protons on $\alpha$-$Me_3Si$ and $\alpha$-$(t$-Bu$)$ groups is not surprising.

The variety of ways in which these and other[2-4,13] long-lived carbon centered radicals (not necessarily containing $Me_3Si$ or $t$-Bu$\cdot$ groups)[13] can be obtained suggests that they are far more ubiquitous in free-radical chemistry than has previously been supposed.

(9) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

(10) See, *e.g.*, H. Fischer in "*Free Radicals*," Vol. 2, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 19.

(11) For a discussion of the conformational effect in substituted ethyl radicals see ref 2, and references cited therein.

(12) For comparison, the less hindered $Me_2\dot{C}CHMe_2$ radical shows a much weaker preference for this conformation (Table I), but the preference does become more pronounced as the temperature is lowered, *i.e.*, $a^{H\beta}$ = 11.9 G at 20° and 9.8 G at −120° (in cyclopropane).

(13) D. Griller and K. U. Ingold, unpublished results.

(14) N.R.C.C. Postdoctoral Fellow 1973-1974.

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## Ozonolysis of *cis*- and *trans*-Diisopropylethylene with Added Oxygen-18 Acetaldehyde

*Sir:*

Three proposals for the mechanism of the reaction of ozone with alkenes in solution have received prominent attention: the Criegee mechanism,[1] the syn–anti zwitterion mechanisms,[2,3] and the aldehyde interchange mechanism.[4] It is well known that aldehydes added to alkene solutions may be incorporated into final ozonides produced *via* ozonization. The alde-

(1) R. Criegee, *Rec. Chem. Progr.*, 18, 11 (1957).

(2) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, 90, 1822 (1968).

(3) (a) R. P. Lattimer, C. W. Gillies, and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 95, 1348 (1973); (b) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *ibid.*, 96, 348 (1974).

(4) (a) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, 88, 3144 (1966); (b) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, 89, 2429 (1967).

hydic oxygen atom will appear in the final ozonide at either the ether or a peroxy site. A zwitterion pathway[1-3] to ozonide formation will result in incorporation of aldehydic oxygen only at the ether site, while the aldehyde interchange pathway will result in peroxy incorporation.

Several workers have used ^{18}O-enriched aldehydes as tracers to distinguish between the two basic pathways to ozonide formation. In these studies the ^{18}O-enriched aldehydes have been added to ozonolysis reaction mixtures, and the site of enrichment of [18]O in the final ozonides produced has been determined either by microwave spectroscopy or mass spectrometry of ozonides or of alcohols obtained by reduction of ozonides. In studies involving low molecular weight alkenes or phenyl alkenes, only ether enrichment has been observed.[5-7] In other studies dealing with larger alkyl alkenes, both ether and peroxy incorporation have been reported.[8-10]

In the first report that indicated substantial [18]O enrichment at the peroxy site, Story, et al.,[8] added [^{18}O]-acetaldehyde in the ozonolysis of trans-diisopropylethylene. The resultant ^{18}O-enriched methyl isopropyl ozonide was reduced with lithium aluminum hydride or methyllithium, and the ethanol and isobutyl alcohol produced were analyzed by mass spectrometry. It was concluded that 68% of the methyl isopropyl ozonide produced in one reaction (and 77% in a second trial) was formed by a pathway which placed the [18]O label at a peroxy site. In the present communication we report results which are in disagreement with this conclusion. In our experiments under reaction conditions similar to those employed by Story, et al.,[8] we have found that most of the [18]O label appears at the ether site in methyl isopropyl ozonide.

Five separate ozonolyses of cis- or trans-diisopropylethylene (99%, Chemical Samples Co.) with added ^{18}O-enriched acetaldehyde (55.0 ± 0.3% by mass spectrometry) were carried out in pentane solvent (99.9%, Chemical Samples Co.). The enriched acetaldehyde had been prepared by exchange with ^{18}O-enriched water.[7]

The alkene and aldehyde concentrations and reaction temperatures are given in Table I. Ozone flow rates

**Table I.** Ozonolyses of Diisopropylethylene with Added Acetaldehyde-[18]O

| Alkene configuration (M) | Alkene concn (M) | Aldehyde concn (M) | Reaction temp (°C) | % total ozonide [18]O enrichment | % ether ozonide [18]O enrichment |
|---|---|---|---|---|---|
| Trans | 0.88 | 0.58 | −78 | 54.6 ± 0.4 | 51.3 ± 1.1 |
| Trans | 0.82 | 0.43 | −95 | 54.7 ± 0.2 | 52.1 ± 0.7 |
| Trans | 1.94 | 1.25 | −111 | 54.4 ± 0.4 | 51.0 ± 1.8 |
| Cis | 1.11 | 0.68 | −78 | 54.6 ± 0.5 | 53.0 ± 0.6 |
| Cis | 0.92 | 0.46 | −111 | 54.7 ± 0.3 | 49.0 ± 0.8 |

(5) S. Fliszár and J. Carles, J. Amer. Chem. Soc., **91**, 2637 (1969).

(6) C. W. Gillies and R. L. Kuczkowski, J. Amer. Chem. Soc., **94**, 7609 (1972).

(7) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, J. Amer. Chem. Soc., **96**, 1536 (1974).

(8) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, J. Amer. Chem. Soc., **90**, 1907 (1968).

(9) R. W. Murray and R. Hagan, J. Org. Chem., **36**, 1103 (1971).

(10) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, J. Amer. Chem. Soc., **93**, 3042 (1971).

employed were ~0.13 mmol/min; reactions were carried out to ~80% completion based on alkene. The ozonides were separated from solvent after fast warm-up[11] using low temperature vacuum distillation; ozonide products were trapped at −63°. Gas chromatographic techniques were used to separate methyl isopropyl ozonide from diisopropyl ozonide.

Mass spectrometry[7] was used to determine the site of ^{18}O-enrichment in the methyl isopropyl ozonide product. An AEI MS-902 mass spectrometer was used with an ionizing voltage of 70 V and a source temperature of 50-80°. The total [18]O enrichment was obtained from the molecular ion. The (MeHCOCH-i-Pr)+ ion was observed (loss of $O_2$) and used to determine the ether [18]O enrichment. Relative intensities of the mass peaks in the regions of interest are given in Table II. The molecular ion (m/e 132) and ether frag-

**Table II.** Relative Intensities of Mass Peaks of Unenriched Methyl Isopropyl Ozonide

| | | | | m/e | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 134 | 133 | 132 | 131 | 130 | 102 | 101 | 100 | 99 | 98 |
| 1.0 | 7.8 | 100 | 9.0 | 0.3 | 0.1 | 0.7 | 8.7 | 4.0 | 0.6 |

ment ion (m/e 100) were by no means the strongest peaks in the spectrum. These peaks were much weaker than the fragment ions at m/e 89, 72, 56, and 44. Spectra of ^{18}O-enriched ozonides were analyzed using procedures described previously.[7] The total and ether [18]O enrichments for the various ozonide samples are given in Table I. The uncertainties listed were determined from at least ten traces for the 134/132 (parent ion) pairs, while at least 20 traces were analyzed for the weaker 102/100 (MeHCOCH-i-Pr)+ pairs. The standard errors were calculated at the 90% confidence level.

The results in Table I indicate that in each of the ozonolyses studied, nearly all of the [18]O enrichment occurs at the ether site. In each trial, however, there is a small difference between the enrichment of the parent ion and the ether fragment ions. One explanation for this difference would be that a small amount of peroxy [18]O incorporation has occurred, either through the aldehyde interchange pathway[4] or some other mechanism.[12] In support of this explanation, the differences in total vs. ether [18]O enrichment seem statistically significant both individually and collectively for the five runs. Internal checks, such as the good agreement in the total [18]O enrichment for the five trials and the consistent intensity ratios of the 132–100 peaks, are satisfactory. Moreover, in other ozonides similar mass spectral analyses were corroborated by microwave spectroscopy[7]; this lends support to the analysis procedure employed here.

One must be cautious, however, before attaching too great a significance to the small difference in total vs. ether [18]O enrichment. The ether fragment mass peaks are quite weak compared to the parent and several of the major fragment ions.[13] Also, other peaks of un-

(11) R. W. Murray and R. Hagen, J. Org. Chem., **36**, 1098 (1971).

(12) One possibility has been suggested by S. Fliszár and J. Carles, Can. J. Chem., **47**, 3921 (1969).

(13) The weak intensity for the M − 32 ions (and sometimes the parent ions) for heavier aliphatic ozonides has been previously noted by other workers.[9,14] This is in contrast, however, to the results for ethylene, propylene, and 2-butene ozonides[7] which have more prominent parent and M − 32 ions.

known origin occur in the spectra with intensities equal to a few per cent of the ether fragment, and one cannot discount the possibility that the small apparent difference in total *vs.* ether [18]O enrichment is due to an unknown fragment or impurity in the spectrum. It would require further very careful work to more unambiguously establish whether or not the small apparent peroxy [18]O incorporation is real.[15]

In any case, our principal conclusions seem well founded. The mass spectral results show that nearly all of the aldehydic oxygen is incorporated at the ether site in the final ozonide; this supports a zwitterion pathway. The upper limit for processes that produce peroxy [18]O incorporation, such as the aldehyde interchange pathway, is about 10% in our runs.[16] These results indicate therefore that such an alternative pathway for the formation of methyl isopropyl ozonide from diisopropylethylene is considerably less important than previously supposed.[8] The reason that our results differ from those reported earlier by Story, *et al.*,[8] is not clear. Reaction conditions were similar in both studies. We have, in fact, employed lower reaction temperatures than those used previously, and a nonzwitterion pathway should become more important as the reaction temperature is decreased.[11] The notable difference is that our analysis dealt with the ozonides themselves while the previous study determined the [18]O enrichment in alcohols derived from the ozonides; this latter procedure is therefore less direct.[17]

**Acknowledgment.** This work was partially supported by a grant (GP 38750X) from the National Science Foundation. Assistance from Margaret Lathrop Johnson in the mass spectral analyses is appreciated.

(14) M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Org. Mass Spectrom.*, **9**, 297 (1974).

(15) For example, if a small correction (7%) is made to the $m/e$ 100 fragment based on the small peak observed at 98 (loss of $H_2O_2$), the values for percent ether [18]O enrichment become 53.2, 54.1, 52.8, 55.1, and 50.7%. A difference between total and ether [18]O enrichment is then no longer clearly apparent for four runs. We have been reluctant to prefer these values since it is not entirely certain that the small mass 98 peak originates from ozonides. Further work is necessary on this point.

(16) The figure of 10% is estimated from the last run in Table I. Extrapolation of that run to 100% [18]O enrichment in the ozonide leads to about 90% [18]O ether enrichment.

(17) C. E. Bishop and P. R. Story, *J. Amer. Chem. Soc.*, **90**, 1905 (1968).

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## A New Hypothesis Concerning the Reactive Species in Carcinogenesis by 7,12-Dimethylbenz[a]anthracene. The 5-Hydroxy-7,12-dimethylbenz[a]anthracene–7,12-Dimethylbenz[a]anthracen-5(6H)-one Equilibrium

*Sir:*

Previous attempts[1,2] to isolate and characterize 5-hydroxy-12-methylbenz[a]anthracene (1) and 5-hydroxy-7,12-dimethylbenz[a]anthracene (2) have failed to yield either 1 or 2, although the presence of 1 and 2 was inferred because of conversions of crude reaction products

(1) W. M. Smith, Jr., E. F. Pratt, and H. J. Creech, *J. Amer. Chem. Soc.*, **73**, 319 (1951).

(2) Unpublished results in the Ph.D. Thesis of C. C. Davis, Ohio State University, 1966.

into the corresponding amino derivatives by the Bucherer reaction.[1] The formation of **2** on mild acid hydrolysis of 5,6-dihydro-7,12-dimethylbenz[a]anthracene 5,6-epoxide (3) was claimed,[3] but no melting point or other analytical data on this compound were reported.

In our attempts to prepare **2** we have found that the compound exists as a mixture of 7,12-dimethylbenz[a]anthracen-5(6H)-one (4) and the phenolic tautomer **2**. On vacuum sublimation of *cis*-5,6-dihydro-7,12-dimethylbenz[a]anthracen-5,6-diol[4] (5) from acidic alumina we obtained a solid sublimate[5] whose nmr and ir spectra indicated that a mixture (*ca.* 1:1) of ketonic and phenolic substances was at hand.[6] This material (*m/e* 272.1205; calcd 272.1201) gives a red 2,4-DNPH derivative,[5] mp 229–230° dec, in a sealed capillary, on recrystallization from dioxane. In order to tell whether the 5-keto or 6-keto isomer (or a mixture of the two) was present we synthesized 5-methoxy-7,12-dimethylbenz[a]anthracene (6) (nmr, CDCl₃, (CH₃)₄Si, δ 2.78 (s, 3 H, 7-CH₃), 3.13 (s, 3 H, 12-CH₃), 3.90 (s, 3 H, OCH₃), 6.93 (s, 1 H, 6-H)), by a method somewhat better than that described,[1] and 6-methoxy-7,12-dimethylbenz[a]anthracene[7] (7), mp 140–141° (δ 3.13 (s, 6 H, 7- and 12-CH₃), 3.83, 3 H, OCH₃), 6.59 (s, 1 H, 5-H)), and cleaved each by heating with sodium ethylmercaptide in dimethylformamide.[8] The resulting deep red solutions of sodium salts were treated *in situ* with acetic anhydride to yield 5-acetoxy-7,12-dimethylbenz[a]anthracene (8),[5] mp 149–150° (nmr 2.40 (s, 3 H,



1, R = H
2, R = CH₃

5

4

2, X = OH
6, X = OCH₃
8, X = OCOCH₃
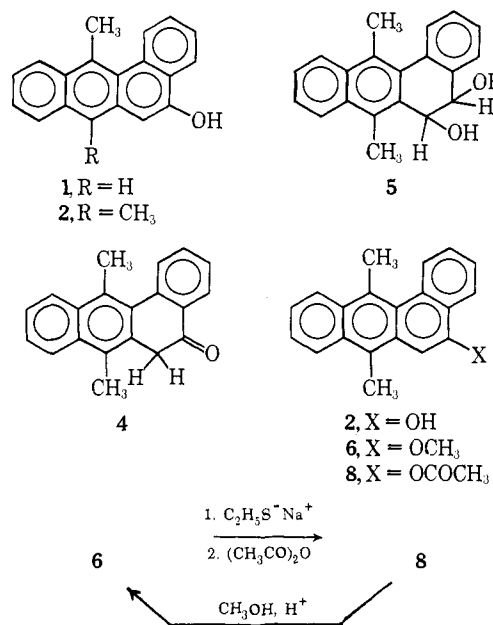
(3) S. H. Goh and R. G. Harvey, *J. Amer. Chem. Soc.*, **95**, 242 (1973).

(4) R. Criegee, B. Marchand, and H. Wannowius, *Justus Liebigs Ann. Chem.*, **550**, 99 (1942); J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948).

(5) All new compounds gave C and H analyses, ir, mass spectra, and nmr data consistent with the postulated structure.

(6) The distinguishing features of the nmr (CDCl₃, (CH₃)₄Si standard) were a broad singlet at δ 5.38 (rel intensity 19) attributed to OH and a singlet at δ 3.62 (rel intensity, 46) attributed to the methylene adjacent to the carbonyl group. The band at 5.38 disappeared within 1 min when D₂O was added. In one experiment the band at 3.62 disappeared in 40 min when the solution was shaken with D₂O–K₂CO₃ solution. The peak at 3.62 reappeared when H₂O was added. In CCl₄ the peaks are at δ 6.17 and 3.67 with relative intensities of 8.6 and 21.2, respectively. In the ir spectrum in CHCl₃, bands at 2.97 μ (OH) and at 5.94 (CO) are noted (3.02 and 5.99 in a KBr pellet).

(7) A description of this work will soon be published.

(8) G. I. Fentrill and R. W. Mirrington, *Tetrahedron Lett.*, 1327 (1970).