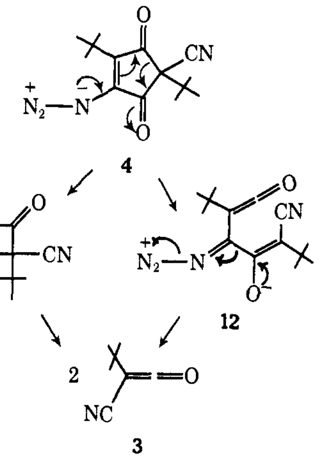
Table I. Spectral Properties of 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone and Synthetic Precursors

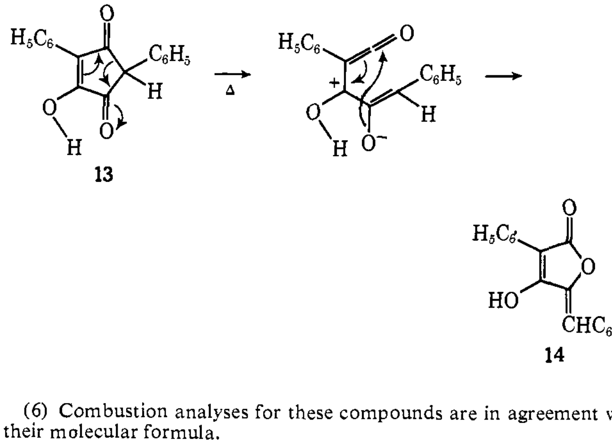
Compd[a]	Mp, °C	Ir (Nujol), cm^{-1}	Nmr[b] ($CDCl_3$), ppm
7	127–128	1700 (C=O) 1600 (C=C)	1.28 (9), s, $-C(CH_3)_3$ 1.37 (9), s, $-C(CH_3)_3$ 4.75 (1), s, -CH 6.47 (1), s, =CH
8	Oil	1680 (C=O) 1660 (C=C)	1.30 (9), s, $-C(CH_3)_3$ 1.46 (9), s, $-C(CH_3)_3$ 6.59 (1), s, =CH
9	Oil	1710 (C=O)	4.87,[c] s, -CH 4.68, s, -CH 1.1, 1.4 (18), $-C(CH_3)_3$
10	68–69	1660 (C=O)	1.45, s, $-C(CH_3)_3$
1	91–92	2110 ($-N_3$) 1640 (C=O)	1.31, s, $-C(CH_3)_3$

[a] Elemental analysis is consistent for assigned molecular formulations. [b] s = singlet, m = multiplet, number in parentheses corresponds to number of protons. [c] The ratio of the δ 4.87 to the 6.48 absorptions is 1:3.4. These absorptions result from the mixture of cis and trans isomers.

4, yield 41%; mp 75–77° dec; ir cm^{-1} (Nujol) 2100 s ($-N_3$), 1750 w, 1690 s (>C=O), 1580 s (>C=C<); nmr δ (C_6H_6) 0.90 and 1.10 ($-C(CH_3)_3$); 5, yield 55%; oil; ir cm^{-1} (Nujol) 2140 s ($-N_3$), 1760 w, 1720 s (>C=O), 1625 s (>C=C<); nmr δ ($CDCl_3$) 1.64 and 1.86 ($-CH_3$).

Thermal decomposition of 200 mg of the cyclopentenedione 4 in refluxing anhydrous benzene gave only *tert*-butylcyanoketene[1] as evidenced by the ir (($\nu_{C=O}$), 2210 cm^{-1} (>C=C=O)) and nmr (δ 0.75, $-C(CH_3)_3$) spectra of the reaction solution. Addition of methanol to the reaction solution gave a quantative yield of α-cyano-α-*tert*-butylmethyl acetate.[1]





These results strongly suggest the mechanism **1** → **4** → **3** for the pyrolytic conversion of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) to *tert*-butylcyanoketene.[1] The first step is an example of the known thermal ring contraction of monoazidoquinones.[7] In fact, 2-cyano-4-azido-2,5-di-*tert*-butyl-1,3-cyclopentenedione (**4**) can be detected (tlc) and isolated in low yield when 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) is partially decomposed in refluxing benzene. The previously unobserved cleavage of 4-azido-1,3-cyclopentenedione (**4**) to cyanoketenes is a new reaction and warrants further study. Two intriguing possible pathways for this facile fragmentation would be either a concerted ring contraction to the ketene dimer **11** which then dissociates to ketene **3** or an electrocyclic ring opening of **4** to a zwitterionic intermediate **12** followed by cleavage to the cummulene. An analogous electrocyclic ring opening may be involved in the pyrolytic rearrangements of certain 1,3-cyclopentenediones to γ-alkylidine(or arylidine)-$\Delta^{\alpha,\beta}$-butenalides, *e.g.*, 2,6-diphenyl-5-hydroxy-1,3-cyclopentenedione (**13**) → pulvinone (**14**).[8]

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(6) Combustion analyses for these compounds are in agreement with their molecular formula.

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Isolation of an Isomeric Form of the Compound of Empirical Composition $[(CH_3)_3Si]_2Fe(CO)_4$

Sir:

All compounds of the type $R_2Fe(CO)_4$ (R = C_2F_5,[1] C_3F_7,[1] SiH_3,[2] $SiCl_3$,[3,4] $Si(C_2H_5)_3$,[4] $Ge(C_2H_5)_3$,[4] $GeCl_3$,[5] $GeBr_3$,[5] GeI_3,[5] $Sn(CH_3)_3$,[6,7] $Sn(C_2H_5)_2Cl$,[7] $Sn(C_4H_9)_2Cl$,[7] $Sn(C_6H_5)_3$,[8] $SnCl_3$,[5] $SnBr_3$,[5] $Pb(C_2H_5)_3$,[6] $Pb(C_6H_{11})_3$,[9] or $Pb(C_6H_5)_3$[9]) described in the literature have either been reported as, or have been assumed to be, monomeric species having octahedral coordination about the iron. Analogously, compounds such as $R(H)Fe(CO)_4$ (R = H_3Si,[2] Cl_3Si,[10,11] or $(C_6H_5)_3Si$[11]) have been described as monomeric, octahedral species containing an Fe–H bond. We have recently synthesized new compounds of the empirical composition $[(CH_3)_3Si]_2Fe(CO)_4$ and $(CH_3)_3Si(H)Fe(CO)_4$, both of which we believe are dimers. Spectroscopic and chemical evidence are consistent with their having a basic tetrahedral frame-

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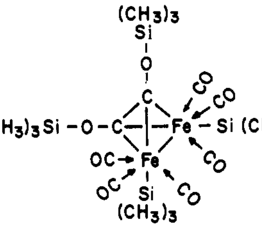
work of two carbon atoms and two iron atoms. This raises the question as to whether at least some of the previously reported compounds mentioned above might not also have this type of structure.

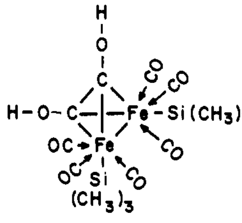
Good yields of the yellow powdery new compound of empirical composition $[(CH_3)_3Si]_2Fe(CO)_4$ (mp 118–120°) were obtained by the reaction of $(CH_3)_3SiI$ with $Na_2Fe(CO)_4$ in tetrahydrofuran.

Anal.[12] Calcd for $[\{(CH_3)_3Si\}_2Fe(CO)_4]_2$, *i.e.*, $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$, $C_{20}H_{36}Si_4Fe_2O_8$: C, 38.21; H, 5.78; Fe, 17.77; I, 0.00; Si, 17.87; mol wt 628.6. Found: C, 38.68, 37.71, 38.84, 38.06; H, 5.73, 5.40, 5.47, 5.58; Fe, 17.05, 17.29, 17.31; I, 0.08; Si, 17.57; mol wt (cyclohexane) 629, 631; (chloroform) 630.

The structure of this compound[13] which is most consistent with its spectroscopic and chemical properties is that given by I. This gives each iron the effective atomic number of krypton. Its infrared spectrum in the CO stretching region (2066 (s), 2022 (vs), 2000 (vs), 1976 (vs), 1962 (sh), 1934 (m) cm^{-1}) is not inconsistent with this structure. The remainder of the spectrum, particularly those bands in the Si–O–C stretching region (1228 (m), 1098 (s), 986 (s) cm^{-1}),[14] is consistent with the above structure. I has two peaks in the ^1H nmr spectrum of exactly equal intensity in the $(CH_3)_3Si$ region (τ 9.66, 9.73) which show no change on heating to 110°. When a solution of I in cyclohexane was treated with excess anhydrous HCl at room temperature, a light yellow solid compound having an empirical composition which would correspond to any of the three compounds $(CH_3)_3Si(H)Fe(CO)_4$, $[(CH_3)_3SiFe(CO)_4]_2$, or $[(CH_3)_3SiFe(COH)(CO)_3]_2$ (II) precipitated, and exactly half the $(CH_3)_3Si$ groups were liberated as $(CH_3)_3SiCl$.



I



II

Anal.[12] Calcd for $[(CH_3)_3SiFe(COH)(CO)_3]_2$, *i.e.*, $C_{14}H_{20}Si_2Fe_2O_8$: C, 34.72; H, 4.17; Fe, 23.07. Found: C, 35.11, 34.49; H, 3.15, 4.02; Fe, 22.90, 23.12.

The data given below suggest that structure II is the preferred one for this compound, even though it was not sufficiently soluble in any appropriate solvent to obtain a molecular weight. Compound II could be formed from I according to

$$[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2 + 2HCl \longrightarrow [(CH_3)_3SiFe(COH)(CO)_3]_2 + 2(CH_3)_3SiCl$$

The cleavage of the O–Si but not the Fe–Si bond is consistent with the observations that the O–Si bond in $n\text{-}C_4H_9\text{–}O\text{–}Si(CH_3)_3$ is cleaved by HCl,[15] whereas the Mn–Si bond in $(CH_3)_3Si\text{–}Mn(CO)_5$ is not cleaved by HCl,[16] and that the Co–Si bond in $(CH_3)_3Si\text{–}Co(CO)_4$ is cleaved only slowly by HCl.[17]

The infrared spectrum of II (Nujol mull) in the CO stretching region (2064 (s), 2020 (vs), 1990 (vs), 1972 (vs), 1952 (sh), 1932 (m) cm^{-1}) is not inconsistent with the proposed structure; also, the bands attributed to the C–O–Si stretching vibrations in I had disappeared and were replaced by a strong band at 1180 cm^{-1}.[18] Well-defined free-OH (3596 (w), 3578 (w) cm^{-1}) and hydrogen-bonded OH stretching vibrations (3488 (sh), 3382 (m) cm^{-1}) were present in the spectrum of II. When DCl was used in place of HCl in the above reaction, the OH stretching vibrations were replaced by the analogous OD stretching vibrations.[19] The ^1H nmr spectrum of II shows only one peak (in the $(CH_3)_3Si$ region) at τ 9.70. No Fe–H peak was observed.

When II was treated with excess $(CH_3)_3SiCl$ and $(CH_3)_3N$ (as an HCl scavenger), compound I was regenerated.

$$[(CH_3)_3SiFe(COH)(CO)_3]_2 + 2(CH_3)_3SiCl \xrightarrow{(CH_3)_3N} [(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2 + 2HCl$$

Compound I begins to undergo very slight thermal decomposition when heated *in vacuo* for 1 hr at 225°. Its reactions with various reagents, *e.g.*, oxygen, water, methanol, trimethylamine, trimethylphosphine, $[(n\text{-}C_4H_9)_4N]Cl$, etc., are consistent with the proposed structure and with the chemical properties of $(CH_3)_3SiFe(CO)_2(\pi\text{-}C_5H_5)$ reported previously.[20]

The properties of certain $(R_3Si)_2Fe(CO)_4$ and $R_3Si(H)Fe(CO)_4$ species previously described in the literature are currently being examined in order to ascertain whether any of them have structures similar to those of the compounds described above.

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[12] Several samples from completely different preparations were employed in the analyses and molecular weights (by osmometry) which are reported.

[13] A single-crystal X-ray examination of $[\{(CH_3)_3Si\}_2Fe(CO)_4]_2$ is currently being carried out in this department by Professor Jerry Donohue.

[14] $(CH_3)_3SiOC(CH_3)_3$ shows bands at 1206 (vs), 1060 (vs), 1029 (vs), 939 (vs) cm^{-1}: E. W. Abel, *J. Chem. Soc.*, 4406 (1960). $(OC)_5CrC(CH_3)OSi(CH_3)_3$ has bands at 1100 (s), 975 (m) cm^{-1}: E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **12**, P1 (1960).

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[16] A. G. MacDiarmid and A. D. Berry, unpublished observations, 1969; A. D. Berry, Ph.D. Thesis, University of Pennsylvania, 1970.

[17] A. G. MacDiarmid and W. M. Ingle, unpublished observations, 1970.

[18] A strong band associated with the COH groups in saturated tertiary alcohols falls in the 1124–1208-cm^{-1} region: R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 85.

[19] The average ν_{OH}/average ν_{OD} ratio = 1.35. The corresponding ratios for the $H_2O\text{–}D_2O$ and $CH_3OH\text{–}CH_3OD$ systems are both 1.35: G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1962, pp 280–282, 334–335.

[20] M. A. Nasta and A. G. MacDiarmid, *J. Organometal. Chem.*, **18**, P11 (1969).

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