Chemiluminescent and Non-Chemiluminescent Ozonations of Selected Electron-Rich Alkynes in Halomethanes

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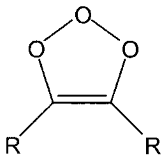
Dedicated to Prof. Dr. Dr. *Theophil Eicher* on the occasion of his 68th birthday

Alkynes of sufficiently high nucleophilicity react with electrophilic O_3 under conversion of the alkyne function to a vicinal dicarbonyl function. Contrary to earlier investigations with alkylated or arylated acetylene, products of complete C–C cleavage were not found as primary products, and, beyond that, peroxidic reaction products were absent. Trimethylsilylated alkynes reacted with O_3 either by uptake of *two* or *three* O-atoms, but again without C–C cleavage or formation of peroxides. Two particularly electron-rich, symmetrically substituted alkynes revealed strong chemiluminescence during ozonation at low temperature, whereas this behavior was not observed with unsymmetrically substituted alkynes. The results are summarized in terms of a mechanistic discussion.

Introduction. – Ozonations of alkynes have been described [3] [4] far less frequently than those of alkenes. Investigations of mechanistic importance have been described by *Keay* and *Hamilton* [5]. These authors found that perfluorobut-2-yne did not react appreciably with O_3 at $-70°$ in CH_2Cl_2, whereas slow conversion was observed with Ph-substituted alkynes, and fast conversions were observed with acetylene itself and with alkyl-substituted acetylenes. Successful conversions with O_3 yielded peroxidic reaction mixtures that were able to epoxidize cyclohexene. The resulting peroxidic species **1**–**5** are depicted below.



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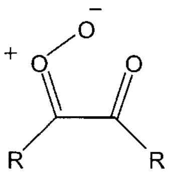

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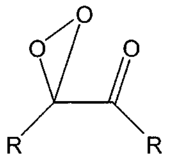

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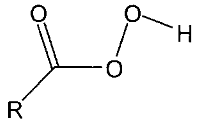

4

Polymeric
peroxides

5

An independent paper of *Jackson* and *Hull* [6] on ozonation of diphenylacetylene published at the same time mentioned 1,2-dioxetane (**6a**) as a possible intermediate because of the indirect chemiluminescence [7] observed during thermal decomposition to **6b** in the presence of fluorescers (*Scheme 1*).

However, structures like **6a** that do not possess a C=O group were earlier ruled out on the basis of IR investigations (C=O group found at 1740 cm^{-1}) by *De More* and *Lin* [8] in the cases of acetylene and its mono- and dialkylated derivatives during

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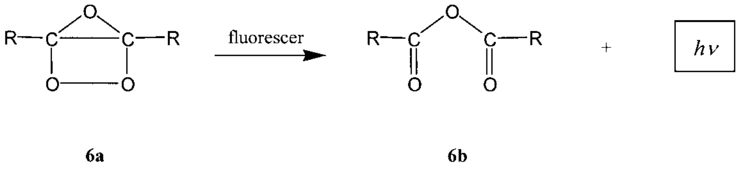
[1] Part of the Ph.D. theses of *H.B.* [1] and *F.W.* [2].

Scheme 1. *Chemiluminescence during Alkyne Ozonation* [6]



ozonolyses in liquid CO_2 at −45°. Later investigations [9] favored structure **6a**, its independent generation *via* photosensitized oxygenation of 2-diazobutan-3-one [10] serving as structural evidence.

In a previous paper [11], we presented the exclusive formation of unsolvated vicinal tricarbonyl compounds during ozonation of ynaminones **7a–e** (*Scheme 2*). In these cases, we found precise 1:1 stoichiometry, complete retention of the C–C bond, and complete absence of peroxidic reaction products in CH_2Cl_2 at −50°. These experimental contradictions of earlier results were traced to the different substitution pattern of the neutral alkyne system, and, therefore, systematic variation in the substitution of **7** and its influence on the experimental results of ozonations was the aim of the present investigations with alkynes **7f–p** (*Table*).

Scheme 2. *Vicinal Tricarbonyl Products of Ozonation of Ynaminones* (*cf. Table*)

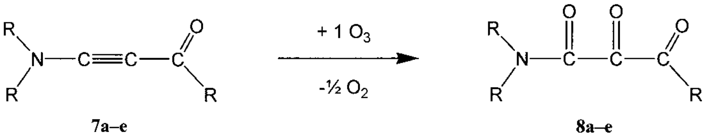
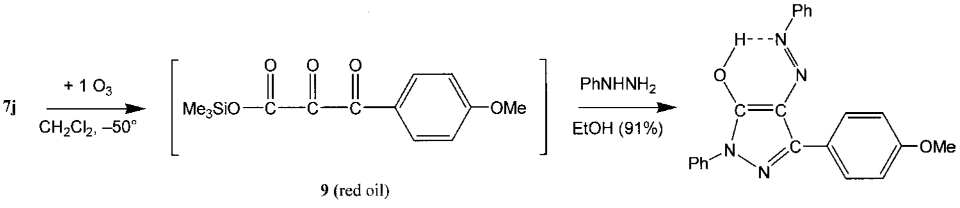


Table. *Disubstituted Alkynes* **7a–e** *and* **7f–p** Used in Previously Reported [11] and Present Ozonations, Respectively

7	R^1	R^2
	$R^1-C\equiv C-R^2$ **7**	
a	(Methyl)(phenyl)amino	4-Methoxybenzoyl
b	(Methyl)(phenyl)amino	4-Chlorobenzoyl
c	(Methyl)(phenyl)amino	4-Nitrobenzoyl
d	Ph_2N	Cyclohexylcarbamoyl
e	(Methyl)(phenyl)amino	*tert*-Butylcarbamoyl
f	EtO	Cl_3CCO
g	Ph	PhCO
h	Ph	4-Chlorobenzoyl
i	Me_3Si	4-Chlorobenzoyl
j	Me_3Si	4-Methoxybenzoyl
k	(Methyl)(phenyl)amino	MeS
l	(Methyl)(phenyl)amino	Me_3Si
m	EtO	Me_3Si
n	$MeOCH_2$	Me_3Si
o	Me_3Si	Me_3Si
p	*t*-BuO	*t*-BuO

Results. – 1. *Exchange of the Amino Substituent of* **7a – e** *for Other Groups Able to Stabilize a Positive Charge.* The alkynes **7f – h** did not react with O_3 under the usual reaction conditions at $-78 - 0°$. Although acyl ethynyl silanes **7i,j** may be viewed as masked ethynyl carbanions, they, in particular **7i**, reacted only very sluggishly with O_3. Therefore, detailed experimental investigations were restricted to **7j** and afforded results outlined in *Scheme 3*.

Scheme 3. *Retention of All O_3 O-Atoms by Trimethylsilyl Derivative* **7j**



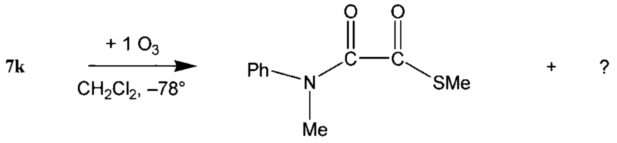
9 (red oil)

10

All O-atoms of O_3, consumed at a stoichiometry of 1 : 1, were introduced to produce the oily red tricarbonyl compound **9**, which was characterized by its IR C=O absorptions (1720, 1660, 1640 cm^{-1}) and was derivatized with excess phenylhydrazine to yield pyrazole **10** (91%).

2. *Exchange of the Acyl Groups of* **7a – e** *for Electron-Releasing Substituents.* Alkyne **7k** could be converted by an equimolar amount of O_3 in CH_2Cl_2 already at $-78°$. TLC Analysis (silica gel; $CHCl_3$) indicated formation of two products that could be easily separated on a short silica-gel column. The main fraction passed unretained through the column to yield **11** as an orange oil (73%), which solidified in part at room temperature. The second fraction became irreversibly adsorbed on the silica gel and could not be extracted without decomposition (*Scheme 4*).

Scheme 4. *Oxalic-Acid Derivative* **11** *from* **7k**



11

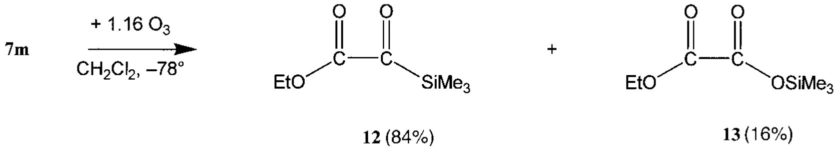
Product **11** was characterized as a saponified derivative of oxalic acid containing only two of the original three O_3 O-atoms, as was observed with **7a – e**.

Alkyne **7l** consumed a molar amount of O_3 in CH_2Cl_2 at $-78°$, but, in this case, a mixture of several products was formed that could not be chromatographically separated without decomposition (TLC analyses). Therefore, further investigations focussed on electron-rich alkynes **7m – p**.

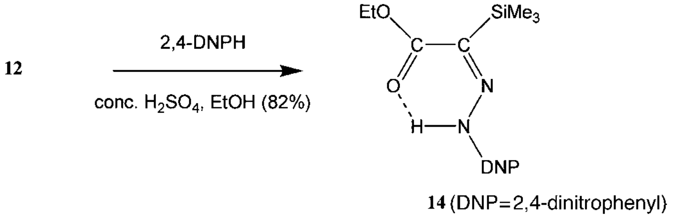
3. *Exchange of Both Substituents of* **7a – e** *Providing Electron-Rich Alkynes* **7m – p**. Ethyl trimethylsilylethynyl ether (**7m**) was ozonized to yield a mixture of ethyl 2-oxo-2-(trimethylsilyl)acetate (**12**) and mixed ethyl trimethylsilyl oxalate (**13**) (*Scheme 5*). The yellow crude mixture of **12** (yellow) and **13** (colorless) became colorless during

introduction of a three- to fourfold excess of O_3; subsequent distillative workup finally afforded colorless oxalate **13**. When the crude reaction mixture was extracted with 10% aqueous $NaHCO_3$, **13** became instantly saponified and could be removed, whereas yellow **12** remained unreacted and could be distilled after drying, and was characterized spectroscopically and by derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) (**14**; *Scheme 6*).

Scheme 5. *Stepwise C–C and C–Si Oxygenations of Alkyne* **7m**

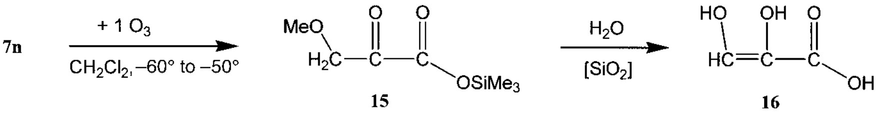


Scheme 6. *Derivatization of the Oxo Ester* **12** *Resistant to Acid Hydrolysis*



Whereas **13**, which contains three O-atoms more than starting alkyne **7m**, was an oxygenation product of two subsequent oxygenation steps, oxo ester **12** contained only two additional O-atoms from the primary ozonation, in analogy to the ozonation products of **7a**–**e**. In contrast to these results, alkyne **7n** took up all three O_3 O-atoms of a molar amount of O_3 during ozonation, as was already observed with **7j** (*Scheme 7*).

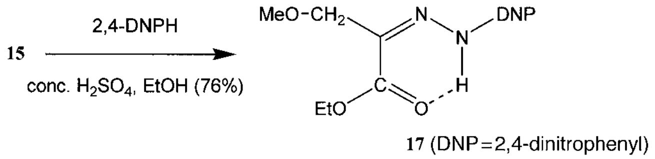
Scheme 7. *Simultaneous C–C and C–Si Oxygenation of* **7n** *by an Equimolar Amount of* O_3



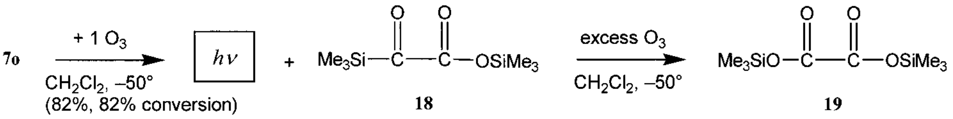
Ozonation product **15** was extremely sensitive towards moisture (analysis by TLC (silica gel) under standard conditions revealed positive reductone tests with *Tillman*'s reagent or methanolic $FeCl_3$ soln. [12]), presumably caused by dihydroxyacrylic acid (**16**) [13]. The yield of **15** was indirectly determined as **17** *via* simultaneous esterification and derivatization by means of a soln. of 2,4-DNPH in conc. ethanolic H_2SO_4 (*Scheme 8*).

Whereas unsymmetrical alkynes **7a**–**n** showed neither direct nor indirect (*i.e.*, in the presence of a fluorescer) chemiluminescence [7] during ozonation [14], symmetrical bis(trimethylsilyl)acetylene (**7o**) revealed an intensely yellow-green chemiluminescence during introduction of O_3 into a soln. of **7o** in CH_2Cl_2 at $-50°$ (*Scheme 9*).

Scheme 8. *Transesterification during Derivatization of* **15**



Scheme 9. *Chemiluminescence during Ozonation of* **7o**



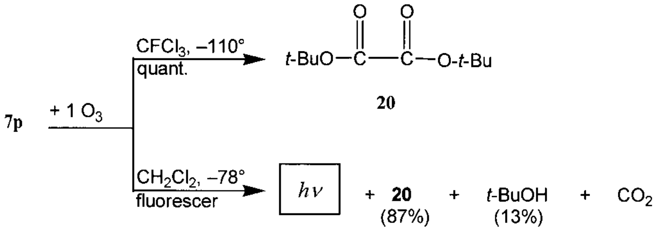
Chemiluminescence stopped after complete consumption of **7o**; the second ozonation step, leading from yellow trimethylsilyl 2-oxo-2-(trimethylsilyl)acetate (**18**) to colorless bis(trimethylsilyl)oxalate (**19**) effected by an excess of O_3 at –50°, did not produce chemiluminescence. Apart from O_3 oxidation of **18**, further tentative conversions were somewhat disappointing. Traces of moisture decomposed **18**, effecting formation of CO and CO_2. A corresponding decomposition was observed with abs. EtOH in the presence of HCl, and ester formation was not detected. Conversion with 2,4-DNPH and conc. H_2SO_4 in abs. EtOH gave rise to a poor yield (6%) of already mentioned 2,4-dinitrophenylhydrazone **14**. Addition of fluoride under non-aqueous conditions similarly led to spontaneous decomposition, before the assumed acylanion intermediate could be trapped by reactive electrophiles.

Despite the structural relatedness of **7o** to di(*tert*-butyl)acetylene, ozonations of these alkynes gave completely different results. *Jenkins* and *Mendenhall* [15] reported that the latter did not show chemiluminescence and that C–C cleavage *and* formation of 1,2-dioxo compound appeared at the same time under various aprotic reaction conditions.

Under these conditions, electron-rich 1,2-bis(*tert*-butoxy)acetylene (**7p**) was ozonized in $CFCl_3$ soln. at –110°. Alkyne **7p** reacted spontaneously with O_3, and it was the aim of this experiment to detect either a dioxirane or a dioxetane as intermediate under these careful conditions, because these species have been purported to be intermediates during ozonation of symmetric alkynes [9][15]. However, even at this low temperature, or with additional cooling to –150° for IR measurement, no reactive intermediates were observed, di(*tert*-butyl)oxalate (**20**) was quantitatively formed, and neither direct nor indirect chemiluminescence [7] was observed. However, this result was solvent-dependent (*Scheme 10*). Ozonation of **7p** in abs. CH_2Cl_2 at –78° led to intensely blue indirect chemiluminescence in the presence of 9,10-dibromoanthracene as fluorescer, while, at the same time, the yield of **20** dropped to 87%, and formation of CO_2 as well as of *t*-BuOH was observed. Comparison with a commercially available sample of di(*tert*-butyl) dicarbonate excluded its formation during ozonation, and thus excludes spontaneous uptake of three O_3 O-atoms.

Discussion. – In summarizing the synthetic results, the following characteristic properties of the investigated alkynes **7a–p** should be stressed: *i*) Only sufficiently

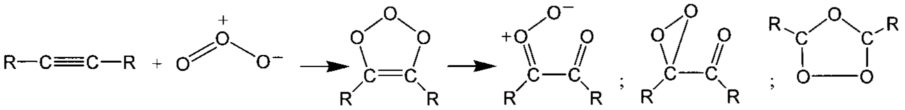
Scheme 10. *Non-Chemiluminescent and Indirect Chemiluminescent Ozonations of* **7p**



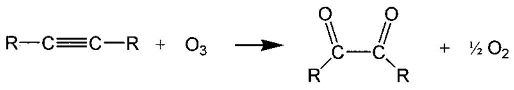
nucleophilic alkynes reacted spontaneously with O_3 at or below $-50°$. *ii*) In most cases, ozonations were rather sluggish, *i.e.*, 10–30% O_3 in O_2 was recovered from the reactions unchanged by trapping with aq. NaI. However, titrations of the I_2 formed compared with the total amount of O_3 introduced affirmed an 1:1 stoichiometry between consumed O_3 and converted alkyne. *iii*) π-Donor substituents of the respective alkyne containing n-electron pairs (R_2N, RO) effected consumption of only two of the three O_3 O-atoms during C=O formations. *iv*) Reaction mixtures warmed to 0° for iodometric titrations did not show any positive peroxide test.

Ozonations of alkynes (*cf.* [3–5][9][15]) are described as 1,3-dipolar cycloadditions of O_3 to C≡C bonds to form initially 1,2,3-trioxoles and subsequently their isomers possessing a cleaved trioxide function (*Scheme 11*). However, this theory is contradicted on the following grounds: *i*) The zwitterionic structure of ground-state O_3, according to *Trambarulo et al.* [16] in 1953 a necessary requirement for a 1,3-dipolar cycloaddition, was ruled out already in 1963 by *Gould* and *Linnett* [17]. Detailed comprehensive calculations by *Harcourt* [18a] confirmed this correction (for experimental arguments, *cf.* [18b]). On the other hand, the observation that alkynes as π-electron donors are able to form charge-transfer complexes with the strongly oxidizing O_3 [3] has recently been claimed for olefins, too [19]. This property should suggest another mechanism involving radical species, as already presented earlier [9]. *ii*) Planar 1,2,3-trioxoles as products of speculative concerted [3+2] cycloadditions of O_3 to alkynes would be antiaromatic species. On the basis of bond-breaking and bond-making energies according to *Scheme 12*, calculated from average bond-dissociation energies, highly exergonic formation of 1,2-dicarbonyl compounds and of molecular O_2 should occur. The high reaction enthalpy is likely to cause formation of highly excited intermediates that would degrade before being observed. Insertion of the third O-atom

Scheme 11. *Classical Proposed Mechanism of Alkyne Ozonations*



Scheme 12. *Concerted Alkyne Ozonation* (*ΔH ca.* -150 kcal mol^{-1})



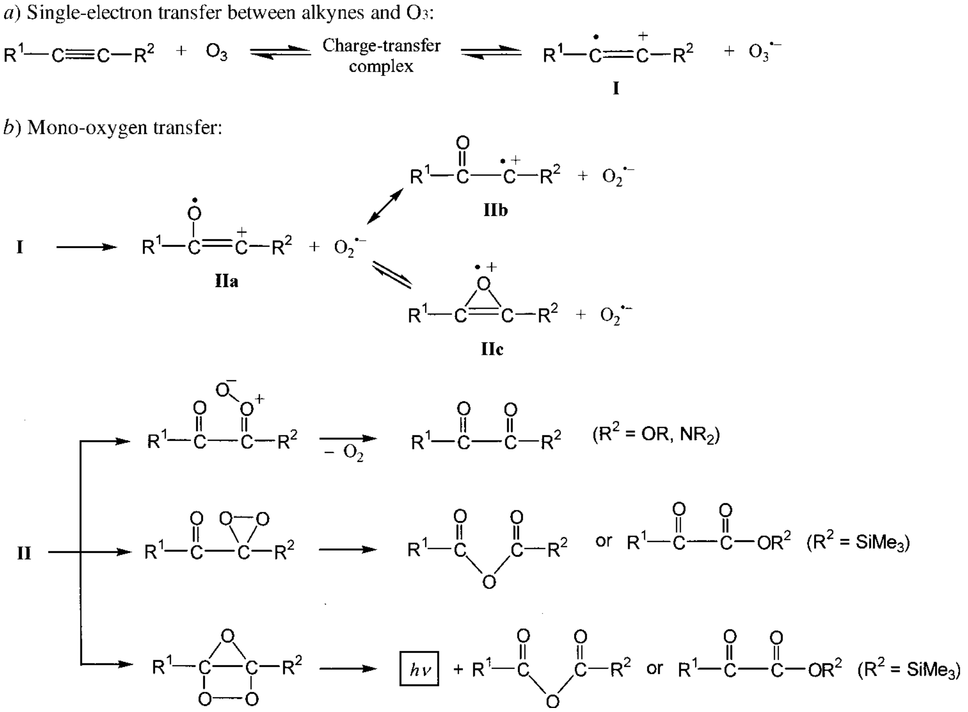
would only additionally enhance the reaction enthalpy. Thus, these 1,2,3-trioxole formations are highly unfavorable. *iii*) It is guessed that 1,2,3-trioxoles form zwitterionic carbonyl oxides, which are claimed to be precursors of dioxiranes and of bicyclic 1,2-dioxetanes in solution. However, the only reported reaction of an actual carbonyl oxide (benzophenone oxide, which is particularly favorably substituted with two Ph groups), carried out by *Griller* and co-workers [20], described a highly exergonic decomposition to yield the carbonyl compound and O_2 (*cf.* [11]). In addition, careful investigations by *Sawaki* and co-workers [21] have shown that 'carbonyl oxides do not isomerize to dioxiranes in solution'.

In summary, there must exist another mechanism by which generation of acyl dioxiranes and bicyclic dioxetanes, which has already been suggested by earlier investigations [5][8][10], can be explained, and which leads to formation of *Baeyer-Villiger*-like oxidation products (not observed here) and chemiluminescence. As an alternative to the generally accepted mechanism, which had been presented at a time when electron-transfer reactions were relatively unknown to organic chemists (*cf.* the prologue of [22]), we propose initial formation of a charge-transfer complex between suitable alkynes (*i.e.*, that possess sufficiently high π-electron density to be able to function as electron donors) and the strong oxidant O_3 [3]. This interaction would represent only a special case of electron-transfer chemistry [23]. The main feature of this mechanism is a considerably enhanced reactivity of the resulting intimate radical ion pair compared to the neutral species. Thus, it has been mentioned recently by *Jansen* and co-workers [24] that even crystalline sodium ozonide (compare the bond distances of O_3 (1.272 Å) and $O_3^{\bullet-}$ (1.34 ± 0.03 Å), see Table 2 in [25]) decomposes at room temperature to yield sodium superoxide and O_2. Such a decomposition with an alkyne radical cation as the counter cation to the ozonide radical anion (radical ion complex **I**) within a charge-transfer complex should lead to O exchange (radical ion complex **II**), expelling superoxide as already suspected [11]. Subsequent bond formations according to classical models (neutralization, radical combination) should lead to the assumed intermediates including regioselective distribution of the three O_3 O-atoms on the two alkyne C-atoms depending on substitution (*Scheme 13*).

With respect to the canonical formula **IIb** and **IIc**, it must be stressed that carbene radical cations have been repeatedly investigated during the last decade [26], and that oxirene radical cations would not be antiaromatic as are their neutral counterparts. Even generation of oxirenes [27] as intermediates, postulated by *Griesbaum* and *Dong* [4], would be possible from **IIc** *via* back electron transfer. Their ozonation has been shown to furnish diacyl peroxides [4]. However, formation of diacyl peroxides from $O_2^{\bullet-}$ and carboxylic-acid derivatives, *i.e.*, anhydrides, is a well-known reaction (see p. 442 in [28]) and would be convincing evidence for intermediately formed $O_2^{\bullet-}$.

A regioselective (**IIa**,**b**) or a symmetric (**IIc**) mono-oxygen transfer should be favored or disfavored by the character of R^1 and R^2. Where $R^2 = OR$, NR_2 n-electrons of heteroatoms preferentially should contribute to a regioselective resonance stabilization of the positive charge. This would concur with our earlier observation [11] that ynaminones yield exclusively vicinal tricarbonyl compounds, when the intermediate carbonyl oxides spontaneously lose an O-atom. In the case of **7p**, bearing two ether moieties, ozonation was found to be solvent-dependent (*cf. Scheme 10*). Radical cations of ynol ethers are well-established species, the distribution of spin

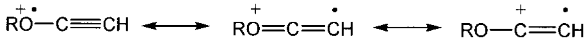
Scheme 13. *Reaction Mechanism Proposed on the Basis of Electron-Transfer Chemistry*



density between O- and C-atom has been determined (see p. 258 in [29] and *Scheme 14*).

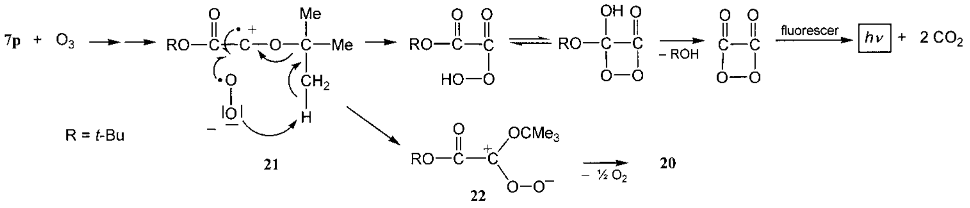
It is known from introductory organic chemistry that solvation of an anion considerably influences its basic or nucleophilic character. The non-polar $CFCl_3$ ($E_T(30)$: 33.3 kcal/mol [30]) is rather poorly solvating whereas CH_2Cl_2 ($E_T(30)$: 40.7 kcal/mol [31]) is considerably more polar. It is assumed that immediate neutralization of radical-ion pair **21** in $CFCl_3$ leads exclusively to carbonyl oxide **22** and its subsequent deoxygenation to afford **20**, whereas, in more polar CH_2Cl_2, this pathway is utilized only to 87%. The remaining 13% should be dominated by the basic character of the solvent-separated $O_2^{\bullet-}$. β-Elimination and subsequent reactions are assumed to yield 1,2-dioxetane-3,4-dione, which is known to exhibit chemiluminescence in the presence of a fluorescer [7] (*Scheme 15*).

Scheme 14. *Spin Distribution between O- and C-Atom in Radical Cations of Ynol Ethers* [29]



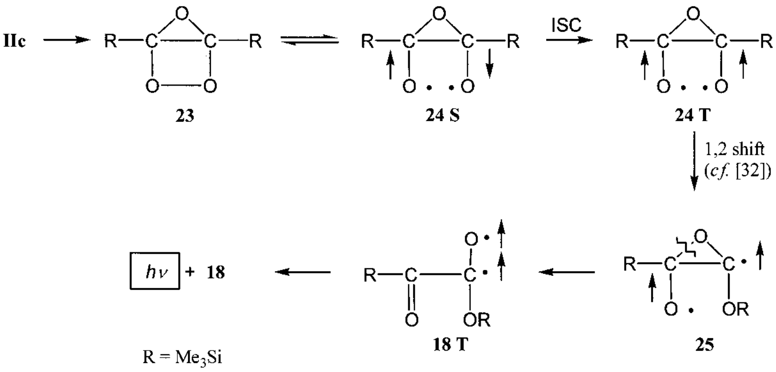
In contrast to **7p**, alkyne **7o** cannot lead to a resonance-stabilized radical cation intermediate, although charge-transfer complexes of organosilicon compounds are known (see p. 155 in [32]), since, in this case, a symmetric intermediate like the non-antiaromatic oxirene radical cation **IIc** (*Scheme 13*) is more probable. [2+2] Cycloaddition should lead to formation of the symmetric 1,2-dioxetane **23** in equilibrium with

Scheme 15. *Tentative Mechanism to Explain Observed Indirect Chemiluminescence during Ozonation of* **7p** *in* CH_2Cl_2



the isomeric singlet diradical **24S** resulting from O–O homolysis. Such diradicals have been proposed by *Pryor et al.* [9], who proved that radicals are intermediates during alkyne ozonations. According to *Hund*'s rule for molecules [33], the SOMOs of such symmetric radical intermediates are of equivalent energy (*i.e.*, degenerate) and consequently should suffer singlet-triplet spin inversion leading to the triplet diradical **24T**. However, the related (trimethylsilyl)methoxyl radical has been described by *Walton* and co-workers [34] to suffer very fast 1,2-C → O silyl migration at low temperature. Joint β-cleavage of the oxirane **25** should then lead to the excited triplet **18T** and, with chemiluminescence, to **18** (*Scheme 16*).

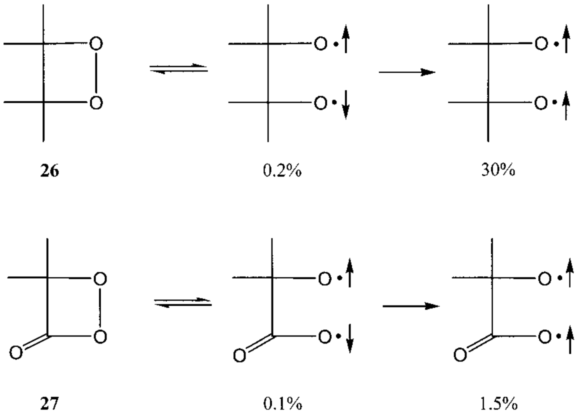
Scheme 16. *Proposal for Direct Chemiluminescence* [7] *during Ozonation of* **7o**



In summary, alkyne **7o** takes up three O_3 O-atoms during 1:1 stoichiometric conversion and reveals strong chemiluminescence. Alkyne **7n** reacts correspondingly but *without* chemiluminescence. Two reasons for the different reactivity can be discussed. Either ozonation of **7n** proceeds preferentially by generation of the isomeric acyl dioxirane (*cf. Scheme 11*) instead of a bicyclic dioxetane because $R^1 \neq R^2$, or O–O homolysis of dioxetane does not follow *Hund*'s rule because of its considerable nonsymmetry. In terms of dissymmetry, a direct comparison of chemiluminescence intensities under identical reaction conditions was published for symmetric tetramethyl 1,2-dioxetane **26** and for nonsymmetric 4,4-dimethyl-1,2-dioxetan-3-one (**27**) (see p. 271 in [7] and *Scheme 17*), where excited singlet and triplet efficiencies depend strongly on the symmetry of the basic dioxetane system.

Conclusion. – The results found during ozonation of alkynes **7** provide evidence that donor-acceptor interactions initiate all oxygenation reactions by O_3. Basically, these

Scheme 17. *Symmetry as a Necessary Condition for Strong Chemiluminescence* [33]



reactions may be described in the context of electron-density flow as has been outlined generally already in 1982 by *Chanon* and *Tobe* [23]. Strong chemiluminescence is assumed to result from a decay of symmetric 1,2-dioxetane intermediates. n-Electron-donor substituents in alkynes **7** prevent uptake of more than two of the O_3 O-atoms consumed stoichiometrically, possibly because carbonyl-oxide intermediates are favored.

Experimental Part

General. The progress of conversions was monitored by TLC: Foils *Alugram® SIL G/UV$_{254}$* and *Polygram® Alox N/UV$_{254}$* from *Macherey & Nagel.* LC Separations were performed on columns of varying lengths: silica gel from *Macherey & Nagel* (0.02–0.05 mm, 70–270 mesh) or from *ICN* (*Silitech*, 63–200 μm). Peroxide analyses: *Merckoquant® 10.011* test sticks, or aq. AcOH/KI, initially on TLC foils, then in soln. CO Analyses: *Dräger Kohlenmonoxid 10/a* tubes. M.p.: standard Cu block or automated with a *Fus-O-Mat.* O_3 Generation in O_2 in a *Fischer 503* ozonizer, gas rate 1 l/min, O_3 concentration 2 mmol/l, *i.e.*, 2 mmol/min. UV/VIS Spectra: *UVIKON 860* from *Kontron*; λ_{max} in nm (log ε). IR Spectra: *Beckman IR-33* or *IR-4230* apparatus; for low-temperature recording, *Variable Temperature Cell 21 000* from *SPECAC* (England). ^{1}H- and ^{13}C-NMR spectra: *Bruker WH 90* and *Bruker AM 400* (^{1}H: 400 MHz, ^{13}C: 100 MHz); chemical shifts δ in ppm, coupling constants *J* in Hz.

Disubstituted Alkynes **7f–p**: *1,1,1-Trichloro-4-ethoxybut-3-yn-2-one* (**7f**) was prepared by conversion of 1-ethoxy-2-(trimethylstannyl)acetylene and Cl_3COCl according to [35]. Aroylations (by benzoyl- or 4-chlorobenzoyl chloride) were unsuccessful.

1,3-Diphenylprop-2-yn-1-one (**7g**) and *1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one* (**7h**) were prepared by acylation of phenylacetylene. *Nef* [36] used its Na salt and PhCOCl, and *Compagnon et al.* [37] used its Li salt and PhCOCN; the Li salt prepared with an equimolar amount of BuLi gave equivalent results with PhCOCl, but was more convenient and generally applicable.

1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-one (**7i**) [38] and *1-(4-methoxyphenyl)-3-(trimethylsilyl)-prop-2-yn-1-one* (**7j**) [39] were prepared from aroyl chloride-$AlCl_3$ complexes and *1,2-bis(trimethylsilyl)acetylene* (**7o**, commercially available, *i.e.*, *Merck*, *Fluka*, *Acros*, *etc.*, prepared according to [38]).

1-[(Methyl)(phenyl)amino]-2-(methylthio)acetylene (**7k**) and *1-[(methyl)(phenyl)amino]-2-(trimethylsilyl)acetylene* (**7l**) were prepared as described in [40] and [41], resp.

1-Ethoxy-2-(trimethylsilyl)acetylene (**7m**) has been used earlier as an effective reagent for mild dehydrative condensations of carboxylic acids and H-acidic materials ([42] and Ref. 2 therein), a convenient method of preparation has been given by *Brandsma* and *Verkruijsse* [43].

3-Methoxy-1-(trimethylsilyl)prop-1-yne (**7n**) was prepared as follows: abs. THF (100 ml) was added to a 2.5M soln. of BuLi in hexane (100 ml, 0.25 mol) under dry N_2. Methyl propargyl ether (see [44], 17.0 g, 0.24 mol) in abs. THF (50 ml) was added dropwise under stirring and cooling to $-78°$. After stirring for 1 h at $-78°$, a soln. of Me_3SiCl (26.4 g, 0.24 mol) in abs. THF (50 ml) was added slowly, the temp. was raised to r.t., and stirring was continued for another h. The soln. was added to ice-water, extracted with Et_2O, the Et_2O phase was shaken with sat. NH_4Cl soln., washed with H_2O, and dried ($MgSO_4$). Fractional distillation afforded **7n** (17.6 g, 52%) as a colorless liquid. B.p. 144°. Characterization was by ^{1}H-NMR spectroscopy and further conversions. ^{1}H-NMR ($CDCl_3$/TMS): 0.25 (*s*, Me_3Si); 3.40 (*s*, MeO); 4.10 (*s*, CH_2).

Commercially available *1,2-bis(trimethylsilyl)acetylene* (**7o**) has been already applied to prepare **7j** [38]. *1,2-Bis(*tert*-butoxy)acetylene* (**7p**) has been prepared according to the procedure described by *Serratosa* and co-workers [45].

Ozonations. Carefully dried O_2 (1 l/min) was passed through the carefully dried ozonizer, the O_3 then through a first safety bottle, the reaction vessel containing the soln. of alkyne **7**, a second safety bottle and a third safety bottle containing a soln. of KI in H_2O/AcOH. After complete conversion of **7** (TLC control), I_2 formed in the third safety bottle was titrated, and absolute consumption of O_3 was determined as the difference of O_3 introduced and O_3 consumed for oxidation of iodide to iodine. It was found that, depending on alkynes **7i**–**p**, 0–60% excess O_3 must be introduced for complete conversion of the C≡C bond, however, alkyne/O_3 stoichiometry was 1:1. Subsequent ozonations to silyl esters (*cf.* [46]) required application of a large excess (3-fold) of O_3; these conversions were very slow. Alkynes **7f**–**h** did not react noticeably even at 0° and are not further considered. Since conversion of **7i** was too sluggish at low temp., ozonation was focussed on the related more reactive alkyne **7j**.

Ozonation of **7j**. An O_3/O_2 stream was bubbled through a soln. of **7j** (4.65 g, 0.02 mol) in abs. CH_2Cl_2 (60 ml) for 16 min (corresponding to 0.032 mol O_3) at $-50°$. After this time, **7j** was completely converted, back titration of formed I_2 revealed a total of 0.02 mol O_3 consumed by **7j**. The yellow soln. was free of peroxides. Dry N_2 was bubbled through the mixture, and the temp. was raised from $-50°$ to r.t. Unexpectedly, the yellow color changed to red at *ca.* $-20°$, however, IR spectra of the yellow and of the red soln. did not reveal noticeable differences. Interestingly, this change in color did not appear in the presence of a small amount of Ph_3P. The solvent of the red soln. was removed *in vacuo*, the remaining red oil of crude *trimethylsilyl 3-(4-methoxyphenyl)-2,3-dioxopropanoate* (**9**) was highly sensitive towards moisture. IR (film): 1720, 1660, 1640. ^{1}H-NMR ($CDCl_3$/TMS): 0.08 (*s*, Me_3Si); 3.85 (*s*, MeO); 6.95, 7.95 (*q*, 4 arom. H, $J_{AB} = 9.7$). Addition of H_2O led to spontaneous evolution of CO and CO_2 (qual. proof) under formation of 4-methoxybenzoic acid; addition of CH_2N_2 in Et_2O equally led to gas evolution and formation of methyl 4-methoxybenzoate.

The soln. of a second batch of **9** was used for derivatization by means of phenylhydrazine at r.t. Phenylhydrazine (5.2 g, 0.05 mol) was added to the soln., and the soln. was stirred for 1 h. The solvent was removed *in vacuo*, and the remaining red oil was crystallized by addition of EtOH (30 ml). The red crystals obtained were filtered by suction, this crude material proved to be the osazone of an ethyl ester (characteristic *t* at 1.15 ppm and *q* at 3.44 ppm). Recrystallization from boiling EtOH afforded red crystals of *5-hydroxy-3-(4-methoxyphenyl)-1-phenyl-4-(phenylazo)pyrazole* (**10**; 6.74 g, 91%). M.p. 173° (dec.). UV/VIS (CH_2Cl_2): λ_{max} 406 (4.65), 261 (4.65). IR (KBr): 3060*w*, 1660, 1635, 1610, 1580*m*, 1555, 1500, 1345, 1265, 1170, 965*s*. ^{1}H-NMR ($CDCl_3$/TMS): 2.15 (*s*, 1 H, disappeared after addition of D_2O); 3.83 (*s*, MeO); 6.97, 8.12 (*q*, $J_{AB} = 10$, 4 arom. H); 7.05–7.44 (*m*, 8 arom. H); 7.85–8.05 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$/TMS): 55.3 (MeO); 114.1, 116.0, 118.8, 123.1, 125.3, 125.9, 127.6, 128.3, 129.7, 138.2, 141.3 (arom. C); 146.4, 158.1 (C=N); 161.1 (C=O of carbonyl tautomer). Anal. calc. for $C_{22}H_{18}N_4O_2$ (370.41): C 71.34, H 4.90, N 15.13; found: C 71.20, H 4.95, N 15.16.

Ozonation of **7k**. A soln. of **7k** (3.54 g, 0.02 mol) in abs. CH_2Cl_2 (60 ml) was ozonized at $-78°$ for 10 min (corresponding to 0.02 mol O_3) as mentioned before. The red soln. obtained was free of peroxides after warming to 20° during introduction of dry N_2. The solvent was removed *in vacuo*, and the oily residue was purified chromatographically on a short silica-gel column with $CHCl_3$. After evaporation to dryness, orange crystals of S-*methyl 2-[(methyl)(phenyl)amino]-2-oxoethanethioate* (**11**; 3.05 g, 73%) were obtained. M.p. 62°. A second unknown product could not be extracted from the column without decomposition.

Data of **11**: IR (KBr): 1660*s* (sh at 1680), 1495, 1380, 1065, 950, 850*m*. ^{1}H-NMR ($CDCl_3$/TMS): 2.25 (*s*, MeS); 3.40 (*s*, MeN); 7.40 (*m*, 5 arom. H). Anal. calc. for $C_{10}H_{11}NO_2S$ (209.37): C 57.37, H 5.30, N 6.69; found: C 57.62, H 5.44, N 6.47.

Ozonation of **7m**. Ozonation of **7m** in CH_2Cl_2 at $-78°$ was rather sluggish. On the one hand, excess O_3 (30%) must be introduced for complete conversion of **7m** under these conditions; on the other hand, *ca.* 16% of the yellow main product *ethyl 2-oxo-2-(trimethylsilyl)ethanoate* (**12**) was oxidized in addition to yield colorless *ethyl trimethylsilyl oxalate* (**13**). The mixture of **12** and **13** could not be separated by fractional distillation. To prepare pure samples of **12** and **13** *via* ozonation, two different procedures were used.

a) *Exhaustive Ozonation*. A soln. of **7m** (2.86 g, 0.02 mol) in abs. CH_2Cl_2 (50 ml) was ozonized at – 78° for 35 min (corresponding to 0.07 mol O_3). Excess O_3 was removed by flushing with dry N_2, and the resulting peroxide-free colorless soln. was fractionated. Colorless **13** (3.38 g, 89%) boiled at 83°/15 Torr ([47]: b.p. 78°/12 Torr).

b) *Ozonation Affording Complete Conversion of* **7m**: A soln. of **7m** (9.0 g, 0.063 mol) in abs. CH_2Cl_2 (60 ml) was ozonized at – 78° for 40 min (0.08 mol corresponding to a 30% excess; 16% O_3 was recovered from the mixture unchanged as determined by oxidation of iodide to I_2). The resulting intensely yellow, peroxide-free soln. was warmed to 20° and extracted with excess 10% $NaHCO_3$ soln. to remove **13**, which is sensitive to hydrolysis under these conditions. After washing (H_2O) and drying ($MgSO_4$), **12** (9.2 g, 84%) was isolated after fractional distillation (finally *in vacuo* and under protection from moisture) as a yellow oil. B.p. 95 – 100°/13 – 15 Torr. UV/VIS (CH_2Cl_2): λ_{max} 443 (1.98) ([48]: UV (cyclohexane): 455 (1.99)). IR (film): 1745, 1715, 1665 ([48]: IR (NaCl): 1740, 1710, 1660), 1250, 850, 760. ^{1}H-NMR ($CDCl_3$/TMS): 0.33 (*s*, Me_3Si); 1.39 (*t*, *Me*CH_2); 4.34 (*q*, Me*CH_2*) ([48]: ^{1}H-NMR (CCl_4/TMS): 0.33, 1.40, 4.27).

Derivatization of **12** *to Give* **14**. A soln. of **12** prepared as mentioned before starting from **7m** (1.4 g, 0.01 mol) in abs. CH_2Cl_2 (50 ml) was concentrated *in vacuo* at r.t. A mixture of 2,4-dinitrophenylhydrazine (4 g, 0.02 mol), conc. H_2SO_4 (15 ml), H_2O (8 ml), and EtOH (40 ml) was added under stirring. The precipitate was isolated and recrystallized from EtOH to afford yellow crystals of *ethyl 2-[(2,4-dinitrophenyl)hydrazono]-2-(trimethylsilyl)acetate* (**14**; 2.9 g, 82%). M.p. 186°. IR (KBr): 3180*w* (NH), 1680*w* (CO). ^{1}H-NMR ($CDCl_3$/TMS): 0.30 (*s*, Me_3Si); 1.43 (*t*, *Me*CH_2); 4.44 (*q*, Me*CH_2*); 8.05 – 8.55 (*m*, 2 arom. H); 9.21 (*s*, 1 arom. H); 14.58 (*s*, NH). Anal. calc. for $C_{13}H_{18}N_4O_6Si$ (354.40): C 44.06, H 5.12, N 15.81; found: C 43.87, H 4.97, N 15.73.

Ozonation of **7n**. A soln. of **7n** (3.50 g, 0.02 mol) in abs. CH_2Cl_2 (60 ml) was ozonized for 12 min at – 60° (corresponding to 0.024 mol O_3, but real consumption by **7n** was only 0.02 mol). The nearly colorless soln. was concentrated at 20° (preliminary peroxide tests were negative); and a soln. of 2.4-dinitrophenylhydrazine (6.0 g, 0.03 mol) in conc. H_2SO_4 (20 ml), H_2O (10 ml), and EtOH (50 ml) was added to the crude pale-yellow oil of *trimethylsilyl-3-methoxy-2-oxopropanoate* (**15**). After stirring at r.t., an orange precipitate of crude *ethyl 2-[2,4-dinitrophenyl)hydrazono]-3-methoxypropanoate* (**17**; 4.96 g, 76%) was formed, after recrystallization from EtOH. M.p. 186°. IR (KBr): 3200, 3120, 1705, 1605, 1580, 1500, 1330, 1300, 1250, 1130, 1090. ^{1}H-NMR ($CDCl_3$/TMS): 1.40 (*t*, $J = 7$, *Me*CH_2); 3.58 (*s*, MeO); 4.38 (*q*, $J = 7$, Me*CH_2*); 8.15 (*d*, $J = 10$, 1 arom. H); 8.45 (*d*, $J = 10$, 1 arom. H); 9.11 (*s*, 1 arom. H); 12.96 (*s*, NH). Anal. calc. for $C_{13}H_{14}N_4O_7$ (326.27): C 44.18, H 4.33, N 17.17; found: C 43.99, H 4.29, N 17.02.

Investigation of **15** by TLC under usual conditions did not reveal simple migration of a single spot. Instead, **15** developed a tail starting from the origin. The whole area of this tail afforded positive reductone tests, presumably due to reductone **16** [13] formed by hydrolysis of **15** on the TLC plate.

Ozonation of **7o**. The end point of complete ozonation of **7o** could be easily recognized due to disappearance of an intensely yellow-green direct chemiluminescence. However, as in the case of **7m**, ozonation was rather sluggish even at – 50°, while, at the same time, overozonation led to quantitative conversion of **7o**.

a) *Exhaustive Ozonation*. A soln. of **7o** (8.50 g, 0.05 mol) in abs. CH_2Cl_2 (60 ml) was ozonized at – 50°, until the soln. indicated a blue color due to unreacted O_3 (85 min, *ca.* 0.17 mol O_3). The temp. was gradually raised to 20° during bubbling dry N_2 through the mixture, until the soln. became colorless. Distillation under exclusion of moisture afforded *bis(trimethylsilyl) oxalate* (**19**; 10.4 g, 89%). B.p. 98°/13 Torr ([47]: 91°/10 Torr; [49]: 96°/10 Torr).

b) *Ozonation Affording Complete Conversion of* **7o**. A soln. of **7o** (8.50 g, 0.05 mol) in abs. CH_2Cl_2 (60 ml) was ozonized at – 50° until the yellow-green chemiluminescence ceased (38 min, 0.075 mol O_3). The total O_3 consumption by the mixture corresponded to *ca.* 0.06 mol. Workup of the yellow mixture (as mentioned before) yielded yellow *trimethylsilyl 2-oxo-2-(trimethylsilyl)acetate* (**18**; 8.95 g, 82%). B.p. 45°/15 Torr, after fractional distillation under exclusion of moisture. UV/VIS (CH_2Cl_2): λ_{max} 450 (1.75), 267 (2.53). IR (film): 1665 (sh at 1690), 1255, 1155, 845, 760, 700. ^{1}H-NMR ($CDCl_3$/TMS): 0.23 (*s*, Me_3SiO); 0.26 (*s*, Me_3SiCO). ^{13}C-NMR ($CDCl_3$/TMS): – 3.1 (*Me_3*SiCO); 0.1 (*Me_3*SiO); 189.4 (Me_3SiO*C*O); 213.8 (Me_3Si*C*O).

Ozonation of **7p**. a) *In $CFCl_3$*. A soln. of **7p** (1.70 g, 0.01 mol) in $CFCl_3$ (40 ml) was ozonized at – 110° (for cooling mixtures between – 78° and – 200°, *cf.* pp. 668 – 669 in [50]) for 5 min (0.01 mol O_3). After this time, **7p** was quantitatively converted. Formation of CO_2 during ozonation was not detected (neither within the escaping gas stream during ozonation nor in the mixture cooled to – 150° in an IR cell). The soln. was free of peroxidic species; the only product formed was *di(*tert*-butyl) oxalate* (**20**). After evaporation to dryness, colorless **20** (2.0 g, quant. yield) crystallized. M.p. 70°, without further purification (*cf.* m.p. 70 – 71° of a sample commercially available from *Fluka*). IR (KBr): 1753, 1731. ^{1}H-NMR ($CDCl_3$/TMS): 1.53 (*s*, 2 *t*-Bu).

b) *In CH_2Cl_2*. Compound **7p** (0.50 g, 3 mmol) and a small amount of 9,10-dibromoanthracene (50 mg) were dissolved in abs. CH_2Cl_2 (5 ml). The soln. was introduced into a small ozonation vessel (18 × 1.5 cm) connected to the variable temp. cell *21000* for IR measurements (*SPECAC*) by a lockable *Teflon* tube. The soln. was cooled to $-78°$. At this temp., **7p** already began to crystallize. An O_3/O_2 mixture was bubbled through the mixture, revealing an intensely blue chemiluminescence with simultaneous formation of CO_2. O_3 Introduction was continued until the crystals of **7p**, separated out on cooling, were dissolved again, and were converted. The major part of the CO_2 generated remained in the cold mixture. Now, the cell was filled by means of a syringe, and the IR spectrum of the soln. was recorded. An absorption corresponding to CO_2 appeared at 2360 cm^{-1} ([51]: 2349 cm^{-1}) together with the strong C=O bands of **20** (1731, 1753 cm^{-1}). Upon warming to 20° and degassing, the typical CO_2 band disappeared. No indication of the C=O absorption of di(*tert*-butyl) pyrocarbonate at 1800 cm^{-1} could be found, *i.e.*, the third O_3 O-atom left the mixture as a gas. After careful removal of the solvent by distillation. ^1H-NMR ($CDCl_3$/TMS) of the residue revealed the proton shifts of **20** (*s*, 1.53) and of *t*-BuOH (*s*, 1.3) in a ratio of 87:13.

REFERENCES

[1] H. Beck, Ph. D. Dissertation, Universität des Saarlandes 1988.
[2] F. Werner, Ph. D. Dissertation, Universität des Saarlandes 1979.
[3] P. S. Bailey, in 'Ozonation in Organic Chemistry', Academic Press, New York, 1982, Vol. II, Chapt. 2, pp. 3–17.
[4] K. Griesbaum, Y. Dong, *J. Prakt. Chem.* **1997**, *339*, 575.
[5] R. E. Keay, G. A. Hamilton, *J. Am. Chem. Soc.* **1976**, *98*, 6578.
[6] S. Jackson, L. A. Hull, *J. Org. Chem.* **1976**, *41*, 3340.
[7] G. B. Schuster, S. P. Schmidt, *Adv. Phys. Org. Chem.* **1982**, *18*, 187.
[8] W. B. De More, C.-L. Lin, *J. Org. Chem.* **1973**, *38*, 985.
[9] W. A. Pryor, C. K. Govindan, D. F. Church, *J. Am. Chem. Soc.* **1982**, *104*, 7563.
[10] W. Ando, H. Miyazaki, K. Ito, D. Auchi, *Tetrahedron Lett.* **1982**, *23*, 555.
[11] K. Schank, H. Beck, G. Himbert, *Synthesis* **1998**, 1718.
[12] K. Schank, *Synthesis* **1972**, 176.
[13] D. B. Sprinson, E. Chargaff, *J. Biol. Chem.* **1946**, *164*, 417.
[14] S. Toby, *Chem. Rev.* **1984**, *84*, 277.
[15] J. A. Jenkins, G. D. Mendenhall, *J. Org. Chem.* **1981**, *46*, 3997.
[16] R. Trambarulo, S. N. Ghosh, C. A. Burrus Jr., W. Gordy, *J. Chem. Phys.* **1953**, *21*, 851.
[17] R. D. Gould, J. W. Linnett, *J. Chem. Soc., Faraday Trans.* **1963**, *59*, 1001.
[18] a) R. D. Harcourt, in 'Lecture Notes in Chemistry' Springer-Verlag, Berlin, 1982, pp. 1–258; b) K. Schank, H. Beck, M. Buschlinger, J. Eder, T. Heisel, S. Pistorius, C. Wagner, *Helv. Chim. Acta* **2000**, *83*, 801.
[19] X.-M. Zhang, Q. Zhu, *J. Org. Chem.* **1997**, *62*, 5934.
[20] F. W. Hardstock, M. Kanabus-Kaminska, D. Griller, *Int. J. Chem. Kinet.* **1989**, *21*, 157.
[21] K. Ishiguro, Y. Hirano, Y. Sawaki, *J. Org. Chem.* **1988**, *53*, 5397.
[22] L. Eberson, in 'Electron Transfer Reactions in Organic Chemistry', Springer Verlag, Berlin, 1987.
[23] M. Chanon, M. L. Tobe, *Angew. Chem.* **1982**, *94*, 27; *Angew. Chem., Int. Ed.* **1982**, *21*, 1.
[24] W. Klein, K. Armbruster, M. Jansen, *Chem. Commun.* **1998**, 707.
[25] R. Gonzales-Luque, M. Merchan, P. Borowski, B. O. Roos, *Theoret. Chim. Acta* **1993**, *86*, 467.
[26] a) D. Bethell, V. D. Parker, *Acc. Chem. Res.* **1988**, *21*, 400; b) T. Bally, S. Matzinger, L. Truttman, M. S. Platz, A. Admasu, F. Gerson, A. Arnold, R. Schmidlin, *J. Am. Chem. Soc.* **1993**, *115*, 7007; c) S. Wo, H. E. Zieger, M. M. Millar, S. A. Koch, *J. Org. Chem.* **1995**, *60*, 5925; d) D. G. Stoub, K.-L. Cheng, J. L. Goodman, *Tetrahedron Lett.* **1996**, *37*, 4927; e) D. G. Stoub, J. L. Goodman, *J. Am. Chem. Soc.* **1997**, *119*, 11110.
[27] E. G. Lewars, *Chem. Rev.* **1983**, *83*, 519.
[28] A. A. Frimer, in 'The Chemistry of Functional Groups: The Chemistry of Peroxides', Ed. S. Patai, Wiley-Interscience 1983, Chapt. 14, pp. 429–461.
[29] J. Iley, P. G. Taylor, in 'The Chemistry of Functional Groups, Supplement E2, The Chemistry of Hydroxyl, Ether and Peroxide Groups', Ed. S. Patai, Wiley-Interscience 1993, Chapt. 6, pp. 241–297.
[30] C. Laurence, P. Nicolet, M. Lucon, T. Dalati, C. Reichardt, *J. Chem. Soc., Perkin Trans. 2* **1989**, 873.
[31] C. Laurence, P. Nicolet, C. Reichardt, *Bull. Soc. Chim. Fr.* **1987**, 125.
[32] V. F. Traven, S. Y. Shapakin, *Adv. Organomet. Chem.* **1992**, *34*, 149.

[33] M. Klessinger, J. Michl, in 'Physikalische Organische Chemie Bd. 3: Lichtabsorption und Photochemie organischer Moleküle', VCH, Weinheim 1990, p. 405.
[34] J. M. Harris, I. MacInnes, J. C. Walton, B. Maillard, *J. Organomet. Chem*. **1991**, *403*, C25.
[35] G. Himbert, L. Henn, *Tetrahedron Lett*. **1981**, *22*, 2637.
[36] J. U. Nef, *Liebigs Ann. Chem.* **1899**, *308*, 264.
[37] P.-L. Compagnon, B. Grosjean, M. Lacour, *Bull. Soc. Chim. Fr.* **1975**, 779.
[38] D. R. M. Walton, F. Waugh, *J. Organomet. Chem*. **1972**, *37*, 45.
[39] N. A. Bychkova, N. V. Zotchik, Z. N. Motorina, I. A. Rubtsov, *Zh. Obshch. Khim.* **1985**, *55*, 1111.
[40] E. Schaumann, J. Lindstaedt, W.-R. Förster, *Chem. Ber*. **1983**, *116*, 509.
[41] J. Ficini, A. Duréault, *C. R. Acad. Sci. Sér. C* **1971**, *273*, 289.
[42] Y. Kita, S. Akai, M. Yamamoto, M. Taniguchi, Y. Tamura, *Synthesis* **1989**, 334.
[43] L. Brandsma, H. D. Verkruijsse, in 'Synthesis of Acetylenes, Allenes and Cumulenes, A Laboratory Manual', Elsevier, Amsterdam, 1981, p. 57.
[44] W. Reppe, *Liebigs Ann. Chem*. **1955**, *596*, 1.
[45] A. Bou, M. A. Pericas, A. Riera, F. Serratosa, *Org. Synth*. **1987**, *65*, 68; *Org. Synth., Coll. Vol. 8*, **1993**, 161.
[46] A. Ricci, M. Fiorenza, A. Degl'Innocenti, A. Seconi, P. Dembeck, K. Witzgall, H. J. Bestmann, *Angew. Chem*. **1985**, *97*, 1068; *Angew. Chem., Int. Ed*. **1985**, *24*, 1068.
[47] H. H. Hergot, G. Simchen, *Synthesis* **1980**, 626.
[48] a) A. Sekiguchi, Y. Kabe, W. Ando, *Tetrahedron Lett*. **1979**, 871; b) A. Sekiguchi, Y. Kabe, W. Ando, *J. Org. Chem*. **1982**, *47*, 2900.
[49] C. Palomo, *Synthesis* **1981**, 809.
[50] H. Kienitz, in 'Methoden der Organischen Chemie (Houben-Weyl-Müller)', 4. Aufl., Bd. 1/2, Thieme, Stuttgart, 1959, pp. 617–761.
[51] M. Hesse, H. Meier, B. Zeeh, in 'Spektroskopische Methoden in der organischen Chemie', 4. Aufl., Thieme, Stuttgart, 1991, p. 45.

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