

Unusual molecules – unusual reactions from tetra-*tert*-butyl-tetrahydrene to the dimer of carbon sulfide

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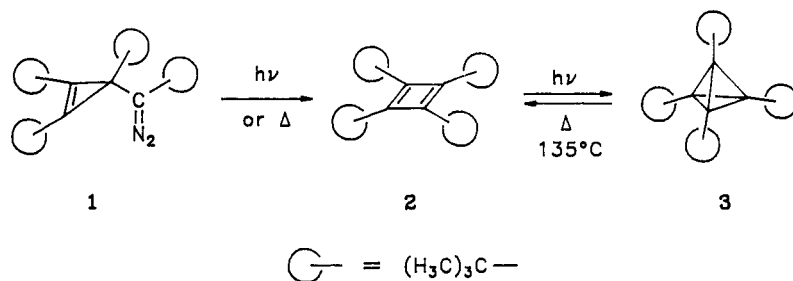
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Abstract: Our perseverance in looking for a second way to prepare tetra-*tert*-butyltetrahedrane has finally been rewarded. By using a similar approach it is also possible to get tri-*tert*-butyl(trimethylsilyl)tricyclo[1.1.0.0^{2,4}]butane – a second, astonishingly stable tetrahedrane derivative.

The attempts to synthesize the parent tetrahedrane required the extensive use of matrix isolation techniques. The skill thus acquired encouraged us to apply this methodology to many other fields, ranging from carbenes, isochalomanes, isofulminic acid and similar species to new cumulenes. For some of the molecules covered in this article (e.g. propargylene 40 or C₅O₂ 44) there is no clear-cut minimum on the potential surface, and these species can be taken as quasilinear. Since it is known that carbon oxides like C₃O and even cyclopropenyli-dene 38 are present in interstellar space, one has to expect that molecules like the carbenes 40 and 41 or compounds such as C₃O₂ 44 or C₄O₂ 46 may also be constituents of the interstellar medium.

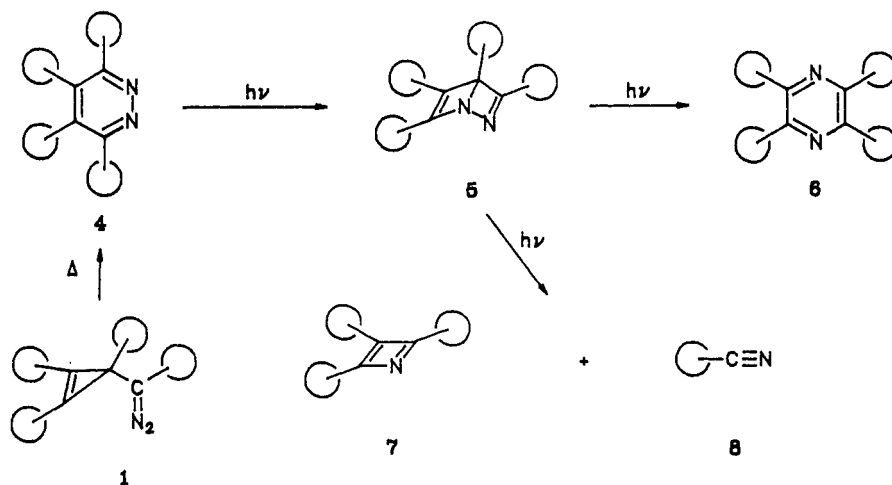
TETRAHEDRANES

The long route which was used twelve years ago (ref.1) to prepare tetrahedrane 3 is very tedious and, because of the low yields of some steps involved, the total amount of the target molecule was small. One attractive alternative was sought in an entry via diazo compound 1. We have found that lithiated *tert*-butyldiazomethane – to our knowledge anions of alkyl-substituted diazomethanes had not been used in organic synthesis so far – reacts with tri-*tert*-butylcyclopropenium tetrafluorobo-

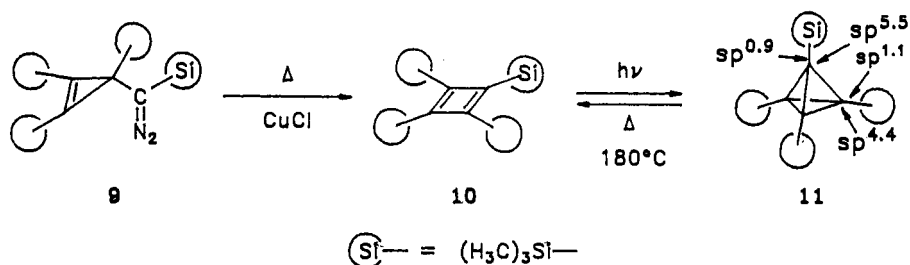


rate with formation of 1 (ref.2). Until very recently we believed that pyrolysis or photolysis of 1 yields di-*tert*-butylacetylene exclusively. In the meantime it turned out that the behavior of the carbene formed in the elimination of nitrogen from 1 is very sensitive to the reaction conditions. If one irradiates 1 with 254 nm light in Rigsolve at 77 K tetrahedrane 3 is formed in 69 % yield (ref.3). It can be shown that cyclobutadiene 2 is an intermediate in the transformation 1→3.

Even pyrolysis (100°C, n-octane as solvent) of 1 gives cyclobutadiene 2 (20%), which can then be isomerized to 3 photochemically, but the main component (60%) from the thermal excitation of 1 is pyridazine 4. This sterically "overcrowded" molecule can be isomerized quantitatively to its Dewar form 5 by irradiation (r.t., $\lambda > 300$ nm). Further photoexcitation (77 K, $\lambda = 254$ nm) of 5 results partly (18%) in a rearrangement of the ring skeleton giving pyrazine 6, but the main reaction pathway (82%) is the fragmentation into tri-tert-butylazete 7 (ref.4) and divalonitrile 8.



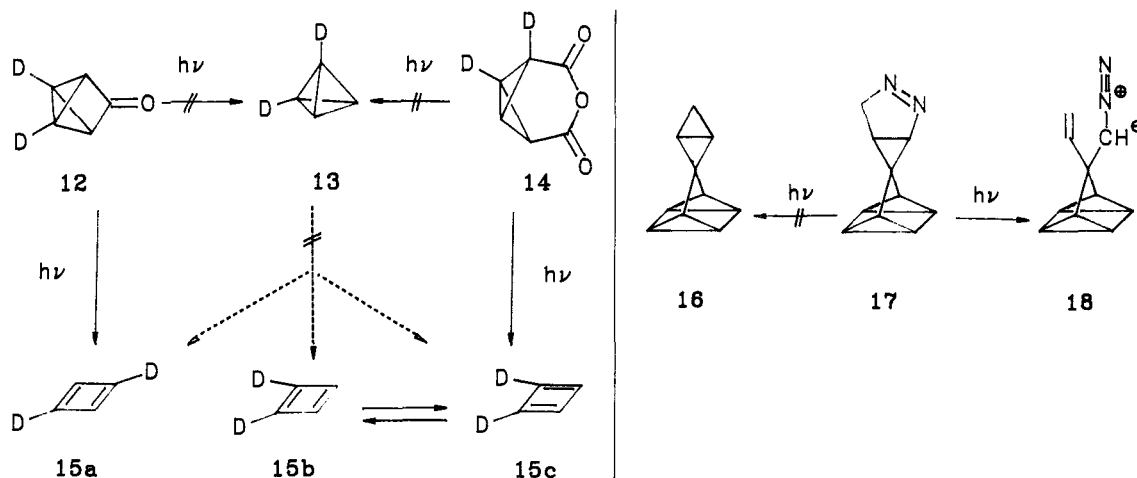
Tetrahedrane 3 owes its thermal stability (back reaction $3 \rightarrow 2$ only at 135°C) to a "corset effect" (ref.1), which should also occur when the tert-butyl substituents are replaced by other bulky groups. This is in fact the case, as can be demonstrated for the example of tri-tert-butyl(trimethylsilyl)tetrahedrane 11. In spite of high ring strain, this molecule is stable up to 180°C (!) (ref.5a). The synthesis of 11 can be



accomplished starting from diazo compound 9, the chemistry of which is unexpectedly diverse similarly to that of 1 (ref.5b). It emerged that cyclobutadiene 10 is formed in the CuCl-catalyzed thermal decomposition of 9, presumably as a CuCl complex. Only after addition of ethylenebis(diphenylphosphane) free 10 can be isolated and finally photochemically transformed into tetrahedrane 11, which melts without decomposition at 162°C. This stability cannot be explained by the "corset effect", which should be smaller in 11 in comparison to 3 (longer C-Si bond). It is the σ -donor- π -acceptor effect of the trimethylsilyl group which stabilizes the tetrahedrane skeleton (ref.6a). The calculated (ref.6b) C(SiH₃)-C bond lengths in silyltetrahedrane are longer (1.479 Å), the other C-C distances are shorter (1.452 Å) than in the parent tetrahedrane (1.477 Å; ref.7). The coupling constants, derived from the ¹³C-NMR spectrum of 11, are in good accordance with those theoretical predictions indicating a distorted tetrahedron. The hybridizations of the C atoms of the skeleton are shown in formula 11 (ref.8).

The unsubstituted tetrahedrane may eventually be stable enough to be isolated in a matrix at 10 K. So in continuation of our former interest in cyclobutadiene we studied all different kinds of potential candidates for the generation of tetrahedrane, which were subjected either to the combination flash pyrolysis/matrix isolation or to matrix irradiation (ref. 1d). Tetrahedrane was never detected.

In order to get eventually some indirect proof to the existence of tetrahedrane, tricyclopentanone 12 (ref.9) and anhydride 14 (ref.10) were irradiated in argon at 10 K. If the dideuteriated tetrahedrane had been an intermediate, the three isomeric cyclobutadienes 15a, 15b and 15c should be formed in the ratio 1:1:1. The experiment shows the opposite result. Ketone 12 gives 1,3-dideuteriocyclobutadiene 15a exclusively. If one starts with 14, only a mixture of the two valence-isomeric species 15b and 15c can be identified. In other words: There is no indication that tetrahedrane 13 is formed in the photolysis of 12 or 14.

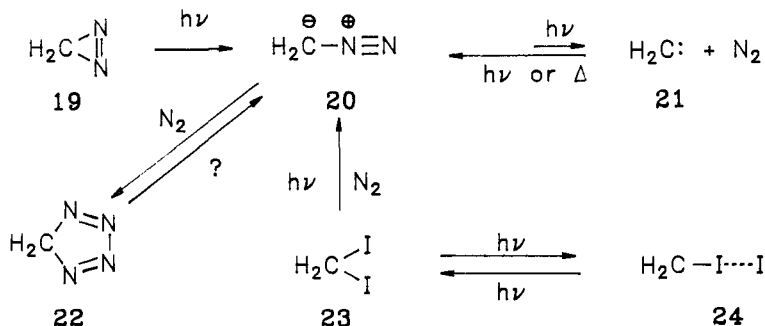


In order to test whether bicyclobutylidene, which is expected as a product in the pyrolysis of polycyclic hydrocarbon 16, might be a suitable precursor for tetrahedrane, azo compound 17 was irradiated in argon at 10 K. To our surprise 17 did not eliminate nitrogen. Diazo compound 18 was formed instead and turned out to be absolutely photostable on further irradiation (ref.11).

CARBENES AND RELATED COMPOUNDS

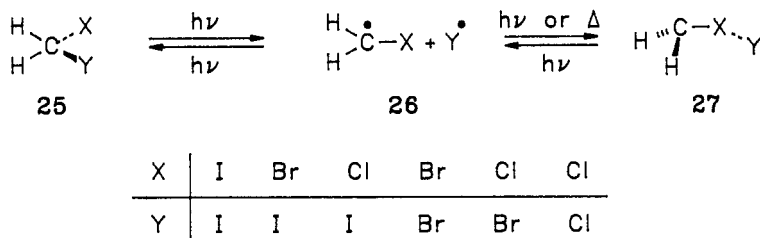
The unusual photostability of 18 has its parallel in the observation that diazomethane 20, which can be easily prepared in argon at 10 K by irradiation of diazirene 19, is also photostable under matrix conditions. This finding is not new. *Pimentel* (ref.12) has already reported that matrix-isolated diazomethane is apparently photostable, due to the fact that methylene 21, formed on photolysis, immediately recaptures the nitrogen, as can be shown by tracer-studies with $^{15}\text{N}^{14}\text{N}$.

In our opinion the nitrogen exchange could also be explained by the intermediate addition of nitrogen to diazomethane itself and final elimination of N_2 from the 5H-tetrazole 22. In order to exclude this possibility we looked for an independent source for methylene, in the hope, that it should give diazomethane when nitrogen is used as the matrix material. This is indeed the case if diiodomethane 23 is irradiated in nitrogen at 10 K.



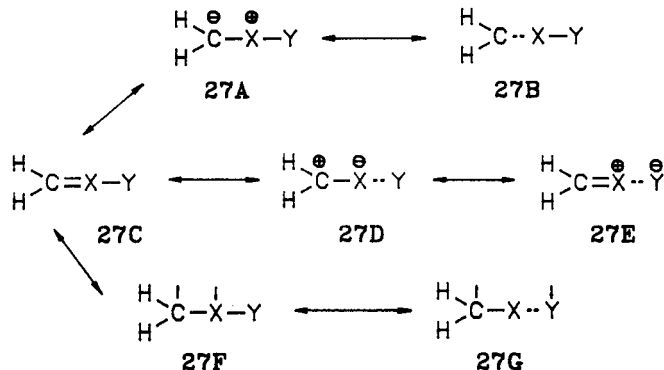
Knowing that, the question arose, what may happen if diiodomethane is photolyzed in an argon matrix. The very first experiment already indicated that under these conditions a new isomer 24 is formed (ref.13).

In the meantime we have studied a whole series of dihalomethanes 25. This enables us to give a broad account of the UV/VIS- and IR-spectroscopic study of the photolysis of halomethanes isolated in rare gas matrices. In all cases (ref.14), and this is even true for tetrachloromethane (ref. 15), the same type of photoreaction occurs, and it appears that the newly formed colored species are always distinct isomers.

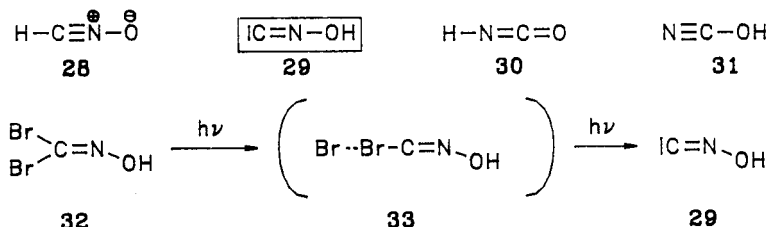


In order to support the experimental results, the IR-spectra of the photoisomers have been studied by ab initio methods (ref.14). There is indeed in all cases an alternative to the tetrahedral arrangement of the four substituents in the halomethanes. As indicated in formula 27 the energy minimum is always connected with a nonplanar C_s geometry. If two different halogen atoms are present in 25, it is the heavier one that migrates. A mechanism that assumes a homolytic cleavage of the weaker one of the two carbon halogen bonds (C-Y) as the primary step can explain the selectivity of the reaction. The radical pair 26 cannot dissociate in the solid matrix and collapses either to educts 25 or products 27.

It is difficult to describe compounds of type 27 with one single structure. Seven possible resonance structures 27A-27G may be considered: 27A symbolizes a halonium ylide, 27B indicates a weak complex between a carbene and halogen, 27C describes a hypervalent species, 27D and 27E can be taken as contact ion pairs, 27F has the double bond of 27C decoupled and 27G describes the molecule as a radical pair. The properties of the isomers 27 show that the resonance structures 27D and 27E are the main contributors to the actual structure.

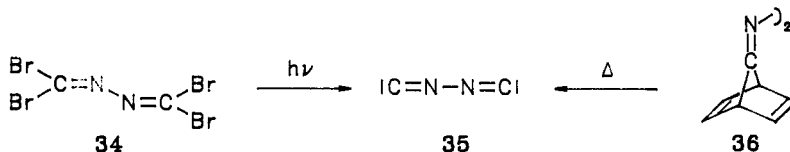


Coming from Gießen, the place of *Liebig*, it makes sense to take advantage of our knowledge about the matrix irradiation of halomethanes in order to solve an old classical problem. Fulminic acid, a molecule beloved by *Liebig* for his whole life, was believed for seventy years to have the carboxime structure 29. When fulminic acid was unequivocally characterized as formonitrile oxide 28 it became a goal to prepare the real carboxime 29 and to complete the list of the four "chemically reasonable" arrangements 28-31 for a compound of the formula CHNO .

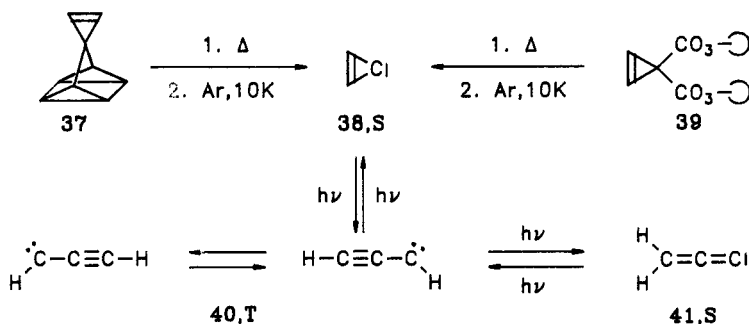


Having in mind the photolability of dibromomethane, dibromoformoxime 32 was irradiated in an argon matrix. On the basis of the observed IR-spectrum and by comparison with the calculated IR bands, it can be shown that photoexcitation of 32 causes not only an isomerization $32 \rightarrow 33$ but also leads to the expected "isofulminic acid" 29 (ref.16).

As a consequence of the successful elimination of bromine from 32 it seemed reasonable to try to prepare diisocyanogen 35 starting from 34. The twofold isonitrile 35 was claimed to be the product in the thermolysis of norbornadiene azine 36 (ref.17). Shortly afterwards (ref.18) it was shown that the compound isolated is in reality monoisocyanogen. A band at 1996 cm^{-1} , which was detected by us in the matrix photolysis of 34 (ref. 19) is more consistent with the calculated stretching vibration of diisocyanogen than the corresponding absorptions of monoisocyanogen at 2294 and 2054 cm^{-1} , which can be found in the matrix-isolated thermolysis product of 36. With the knowledge of the absorption of 35 (1996 cm^{-1}) it is possible to identify this compound as a minor component even in the thermal fragmentation of 36.



As was discussed before, we intended to use quadricyclane derivative 16 as a starting material for bicyclobutylidene. This goes back to the observation that polycycle 37 is an ideal candidate for the thermal formation of cyclopropenylidene 38 (ref.20). The same molecule can be prepared starting from diprester 39 (ref.21). These findings are of potential importance: First, cyclopropenylidene 38, which has a singlet ground state, is now known to be the most abundant hydrocarbon in interstellar space (ref.22). Second, the three possible C_3H_2 isomers 38, 40 and 41 can be transformed into each other photochemically under matrix conditions. The structure of 41 could be elucidated by comparison of the experimental with the computed IR spectrum of singlet vinylidenecarbene 41 (ref.21).

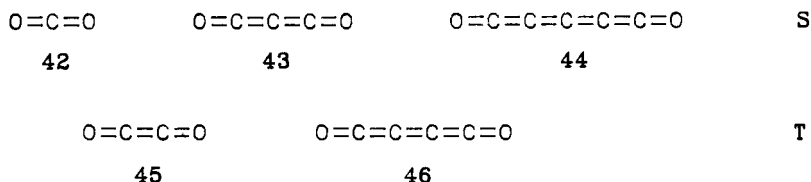


On the contrary the accordance between the observed and calculated IR spectrum of propargylene 40 is very poor as long as an harmonic approximation is used in the theoretical analysis of the vibrational spectrum of triplet 40 (ref.23). The failure of the harmonic treatment suggests that there is no clear-cut minimum on the potential surface of 40. The theoretical spectrum shows a considerable improvement if the two antisymmetric CCH bend and CC stretch frequencies are picked out and treated on the basis of a theoretical unharmonic model and afterwards added to the other seven modes treated in an harmonic approximation. This indicates that propargylene 40 has to be regarded as a quasilinear molecule (ref.23).

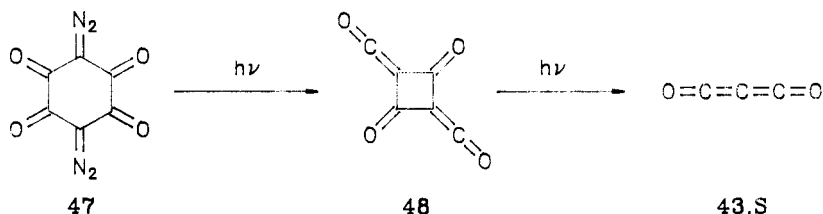
NEW CARBON OXIDES AND SULFIDES

Vinylidenecarbene 41 can be regarded as the connecting link with the last group of unusual molecules, which are all open chain cumulenes.

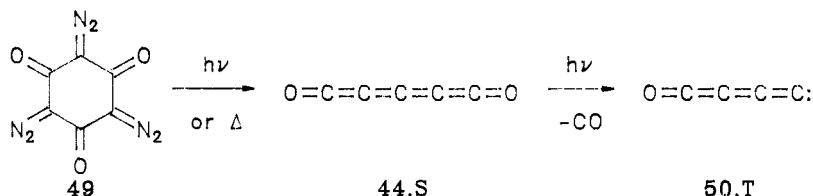
Theory predicts that carbon oxides of the type C_nO_2 should have a singlet ground state if the number of carbon atoms is odd, but a triplet ground state is expected for molecules with an even number of carbon atoms (ref. 24). When we began our studies of compounds 42-46 only carbon dioxide 42 and carbon suboxide 43 were known.



Bis(diazo)ketone **47** undergoes a twofold *Wolff* rearrangement on photoexcitation ($\lambda > 360$ nm) in an argon matrix at 10 K. Further irradiation ($\lambda = 254$ nm) of **48** does not give C_4O_2 , as we hoped, by elimination of two CO molecules, but follows the "normal" pathway, namely the splitting of two ring bonds with the formation of two molecules of C_3O_2 **43**.

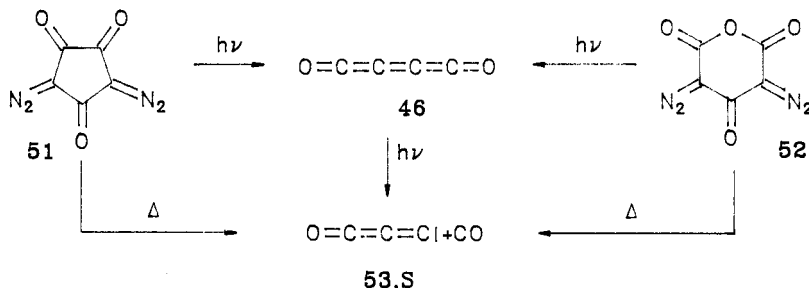


A more amazing result is the loss of carbon monoxide when tris(diazo)ketone **49** is irradiated (ref.25). The sole product is the carbon oxide **44**. The same species C_3O_2 is observed when **49** is subjected to pyrolysis in the gas phase (600-700°C). If **44**, which has a singlet ground state, is condensed together with a low-melting solvent on a cold finger cooled with liquid nitrogen, a solution of **44** may be obtained in which C_5O_2 is astonishingly stable and remains unchanged even after several days at room temperature. Pure **44**, a yellow solid at -90°C , polymerizes above this temperature to give a black graphite-like polymer of the composition C_5O_2 . When matrix-isolated **44** is irradiated with 230 nm light, CO is lost and triplet 4-oxo-1,2,3-butatrienylidene **50** is formed.



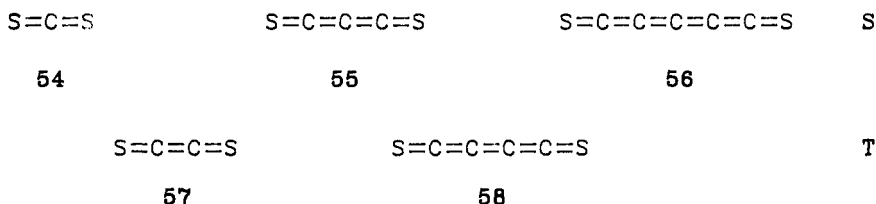
Another aspect (ref.26) is worth mentioning: The high-resolution IR spectrum of the ν_4 band system located at 2242 cm^{-1} indicates that C_5O_2 **44** may be a "super carbon oxide" with two very low-lying vibrations, each of which might exhibit a quasilinear bending potential similar to that of propargylene **40**.

Even more exciting is the compound which originates on matrix irradiation of either ketone **51** or anhydride **52** (ref.27). All spectral data confirm that the isolated species has to be C_4O_2 **46**. In accord with the proposed structure is the photocleavage of **46**, which occurs on irradiation with wavelengths > 300 nm. Under these conditions CO is split off. The compound formed is singlet C_3O **53**, which is also the only product if **51** or **52** is pyrolyzed in the gas phase. So the formal double bond in **46** is broken quite easily on irradiation. This is in agreement with the calculated state correlation diagram for the photolysis of **46** (ref.27).

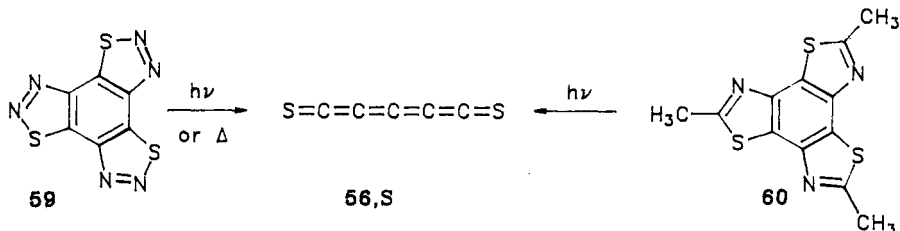


C_4O_2 is the first dioxide of carbon with an even number of carbon atoms. Therefore it is important to know its multiplicity. It might very well be that C_4O_2 possesses a singlet ground state, in contradiction to *Hund's* rule. *Ab initio* calculations carried out by *Janoschek* (ref.28) predict that the singlet state of linear 46 might be very close and only a little higher in energy than the triplet. On bending, the singlet becomes the ground state. Experimentally we cannot make a decision. The IR spectrum of C_4O_2 fits equally to the calculated spectra of 46,S or 46,T, the measured UV spectrum is in better agreement with the theoretical spectrum of 46,T. On the other hand we were unable to detect an ESR signal for 46,T.

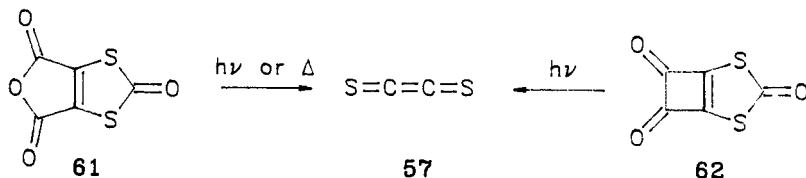
The polymer of C_3O_2 might be of interest as a conducting material. If this is so, the corresponding sulfur containing compound should be even better. Therefore we started a similar study of the sulfides of carbon. CS_2 54 and C_3S_2 55 are known compounds. The other three 56, 57 and 58 remained to be synthesized when we began our studies. C_3S_2 56, as far as we know the heaviest open chain cumulene, can be prepared by 254 nm photolysis or flash pyrolysis of precursor 59 or (in much lower yield) of



60. The IR and UV spectra of 56, are again in accord with the calculated vibrational modes and excitation energies (ref.29). C_3S_2 56 can be kept in solution at $-30^\circ C$ for several days. As expected, solvent-free C_3S_2 gives a black solid on warm-up.



I would like to conclude this report with a remark about some work on C_2S_2 (ref.30), which is still under way in our laboratory. Photolysis of dithiocarbonate 61 in argon at 10 K yields a species which has to be C_2S_2 57, as is indicated by an IR absorption at 1179 cm^{-1} and a very characteristic UV spectrum (362, 368, 376, 384 and 392 nm). On further irradiation, matrix isolated 57 is fragmented into two molecules of CS, providing further proof for the structure of C_2S_2 . Two observations should be added: First, C_2S_2 is stable enough to be detected in the matrix-isolated product of the flash pyrolysis of 61. Second, C_2S_2 can also be prepared by photolysis of squaric acid derivative 62.



It is predicted (ref.24a) that C_2S_2 should possess a triplet ground state. Indeed, when 62 is irradiated it is possible to observe a typical triplet signal in the ESR spectrum, but the pattern of the signal does not fit to 57 with a linear structure. So the question about the multiplicity of 57 remains unanswered. Additional experimental studies are needed. The same is true for the theoretical part: Latest MCSCF calculations, performed again by *Janoschek* (ref.28,31), indicate that the singlet state of linear 57 might be even lower in energy than the triplet. In other words: C_2S_2 might be the first example for the violation of *Hund's* rule in a molecule representing the energy minimum on the potential curve.

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