computationally, and in cyclobutadiene the qualitative predictions and quantitative calculations appear to be in good agreement with the available experimental evidence.

Our work on defining the minimally acceptable wave functions for diradicals whose high symmetry allows a test of the adequacy of different types of calculations should be a useful guide for theoretical studies of systems with lower symmetry. For instance, one would anticipate that π CI will still be essential for obtaining the correct relative energies of $^1A_1$ and $^1B_2$ in trimethylenemethane derivatives where substituents reduce the maximum molecular symmetry from D_{3h} to C_{2v}. Similarly, the Jahn–Teller effects that can be anticipated to occur in the highly symmetrical diradicals discussed here are also useful for understanding the potential surfaces for diradicals in which two states are degenerate by "accident" instead of by symmetry.[47]

In addition to being of methodological use to theoreticians, we hope that our work on diradicals will stimulate experimental attempts to test our computational predictions. The expectation of a short-lived triplet state in cyclobutadiene, the possibility that substitution in singlet trimethylenemethane can result in a planar geometry being lower in energy than an orthogonal one, the prediction of facile pseudorotation in singlet cyclopentadienyl cation, and the suggestion of a singlet ground state for cyclopropenyl anion are but a few of the qualitative results that await experimental verification.

Although we do not claim to have come close to solving the Schrödinger equation for any of the diradicals discussed here, some of the calculations carried out by us and by others on these molecules have been near or at "state of the art" for systems of this size. Consequently, experimental tests of some of our more quantitative predictions, for instance, those regarding the size of the barrier to pseudorotation in cyclobutadiene and in $(NH)_3^{2+}$, should provide information regarding the numerical reliability of results at this level of theory.

Experiments on diradicals are by no means easy to carry out, and those necessary to test some of our predictions may even require the development of new techniques. Nevertheless, given the healthy skepticism of most experimental chemists regarding the relability of calculations, one of the strongest prods to experimental work is to make specific theoretical predictions that can, at least in principle, be tested.

Although the predictive ability of our calculations on diradicals certainly requires further experimental verification, we have established that theory can furnish simple explanations of apparently anomalous experimental results in this area of chemistry. The difference in ground states between cyclobutadiene and cyclopentadienyl cation, two antiaromatic annulenes with isoelectronic π systems, can be understood on the basis of orbital pictures and minimization of electron repulsion. Minimization of Coulombic repulsion between electrons is also responsible for the fact that singlet trimethylenemethane, in contrast to the triplet, prefers an orthogonal geometry. The qualitative importance of the effects of electron repulsion in diradicals is what makes the theoretical study of this type of molecule rich in both interest and challenge.

We gratefully acknowledge financial support of our theoretical studies by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Alfred P. Sloan Foundation, and the Eli Lilly Company.

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[47] E. R. Davidson, W. T. Borden, and J. Smith, *J. Am. Chem. Soc.*, **100**, 3299 (1978); E. R. Davidson, *ibid.*, **99**, 397 (1977).

Valence Bond Isomers of Aromatic Compounds Stabilized by Trifluoromethyl Groups

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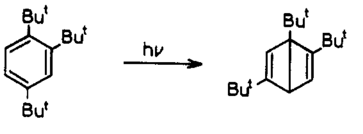
Received April 30, 1980 (Revised Manuscript Received January 5, 1981)

The first synthesis of valence bond isomers of aromatic compounds was carried out in 1962 by van Tamelen and his group,[1] through the isolation of a stable Dewar-type benzene by irradiation of tri-*tert*-butylbenzene (eq 1). Their idea was that the bulkiness of the *tert*-butyl groups would destabilize the flat structure of benzene; if it were converted to the nonplanar Dewar structure, the repulsion between *tert*-butyl groups would be relieved.



(1)

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Itsumaro Kumadaki was born in Kyushu, and received both his undergraduate education and his Ph.D. degree from Kyushu University. He has been on the faculty of Tokyo College of Pharmacy since 1967, where he is now Assistant Professor. He spent the year 1971–1972 at the University of Manchester with R. N. Haszeldine.

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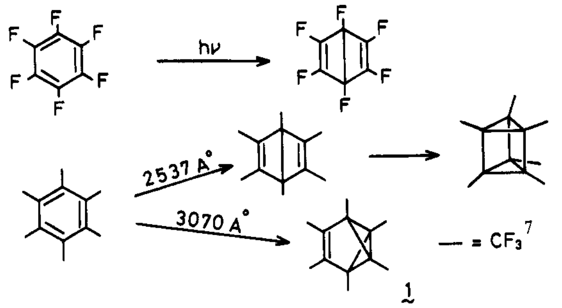
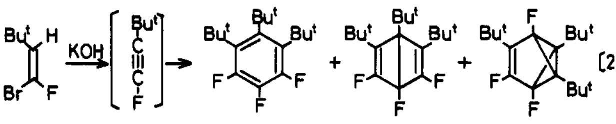
[1] van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1962**, *84*, 3789.

0001-4842/81/0114-0076$01.25/0 © 1981 American Chemical Society

Scheme I



All the valence bond isomers isolated in the following few years contained *tert*-butyl groups (for example, see eq 2).[2] Therefore, one might have surmised that if



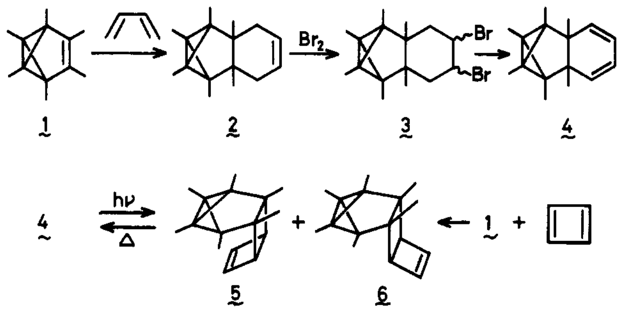
[2]

tert-butyl groups were absent, such valence bond isomers would be too unstable to be isolated from photoreactions.

However, valence bond isomers of fluorinated benzene derivatives are easily isolated from photolysis, as in the examples shown in Scheme I. Hexafluorobenzene gives the Dewar form in a high yield.[3,4] Also, hexakis(trifluoromethyl)benzene gives hexakis(trifluoromethyl)benzvalene by irradiation with a high-pressure mercury lamp or hexakis(trifluoromethyl)Dewar benzene and prismane with a low-pressure mercury lamp[5-7] (Scheme I).

Especially remarkable are the isolation of hexakis(trifluoromethyl)benzvalene in high yield and the high stability of these isomers compared with the hydrocarbon analogues. Lemal et al.[8] carried out thermodynamic and kinetic analyses of the isomerization of valence bond isomers of hexamethylbenzene and its perfluoro analogues and reported that the perfluoro analogues were more stable than their hydrocarbon counterparts. Thus, hexakis(trifluoromethyl)(Dewar benzene) is stabilized by 30 kcal/mol relative to the aromatic isomer when compared with the hexamethyl analogues. They proposed to designate as the "perfluoroalkyl (Rf) effect" the composite of the stabilizing influences of perfluoroalkyl groups on highly strained compounds. They suggested the Rf effect to comprise both thermodynamic and kinetic elements. However, these elements were not fully explained.

Scheme II



We felt at the beginning of our work that the steric effect was not the only factor, since fluorine is nearly as small a substituent as hydrogen and a methyl is nearly as large as a trifluoromethyl group. Further, hexakis(trifluoromethyl)benzene is converted to the benzvalene analogue, but the more strained hexakis(pentafluoroethyl)benzene is not. Other conceivable factors which we could point out were destabilization of π bonds by p–π repulsion between the lone-pair electrons of fluorine atoms and the π electrons of benzene rings, dipole–dipole repulsions between fluoroalkyl substituents, and some effects of highly electronegative fluorine substituents on hybridization in strained carbon frameworks. However, we could not specify these effects in each case. We chose to utilize the Rf effect for the synthesis of new strained ring systems and thereby to understand the Rf effect more deeply.

Our first objective was to utilize the high stability of hexakis(trifluoromethyl)benzvalene toward the synthesis of tetrakis(trifluoromethyl)tetrahedrane. Although the objective tetrahedrane has not yet been isolated, we have obtained some noteworthy results, including the trapping of tetrakis(trifluoromethyl)cyclobutadiene and the isolation of valence bond isomers of an oxepin derivative. A second objective was the synthesis of valence bond isomers of heteroaromatic compounds, again making use of the stabilizing effect of trifluoromethyl groups. We have obtained trifluoromethylated valence bond isomers of pyridine, thiophene, pyrrole, and 1,4-diphosphorin (diphosphabenzene).

Reactions of Hexakis(trifluoromethyl)benzvalene (1) toward Synthesis of the Tetrahedrane

Route through the Diels–Alder Adduct of 1. Compound 1 was synthesized independently by Haszeldine[6] and by Lemal.[5] Haszeldine described its reaction with cyclopentadiene, but neither the stereochemistry of the adduct nor its reactions with other olefins were reported. We have examined its reactions with many dienes and confirmed the structure of its adduct with furan as the exoform by X-ray analysis of its dibromide.[9]

We converted the Diels–Alder adduct of 1 with butadiene to the dibromide 3 and 3 into the diene 4, as shown in Scheme II.[10]

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(2) Viehe, H. G.; Merenyi, R.l; Oth, J. M. G.; Senters, J. R.; Valange, P. *Angew. Chem.* **1964**, *76*, 888, 922.

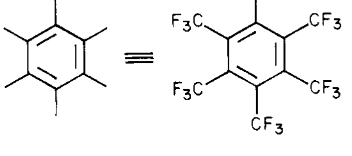
(3) Camaggi, C.; Gozzo, F.; Cevidalli, G. B. *J. Chem. Soc., Chem. Commun.* **1966**, 313.

(4) Barlow, M. G.; Haszeldine, R. N.; Hubbard, R. *J. Chem. Soc., Chem. Commun.* **1969**, 301.

(5) Lemal, D. M.; Staros, J. V.; Austel, V. *J. Am. Chem. Soc.* **1969**, *91*, 3373.

(6) Barlow, M. G.; Haszeldine, R. N.; Hubbard, R. *J. Chem. Soc., Chem. Commun.* **1969**, 202; *J. Chem. Soc. C* **1970**, 1232.

(7) In this Account, CF_3 groups are represented as plain lines in portrayal structures; thus

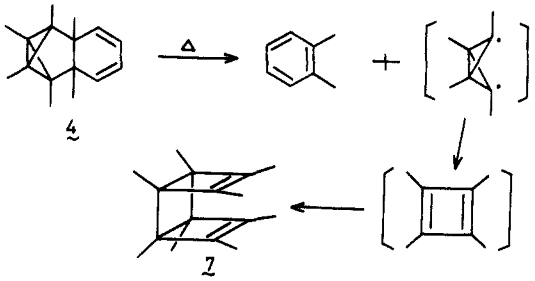


(8) Lemal, D. M.; Dunlap, L. H., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 6562.

(9) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Hanzawa, Y.; Honda, M.; Iitaka, Y. *Tetrahedron Lett.* **1976**, 2545.

(10) Kobayashi, Y.; Kumadaki, I. Ohsawa, A.; Hanzawa, Y.; Honda, M. *Tetrahedron Lett.* **1975**, 3819.

Scheme III

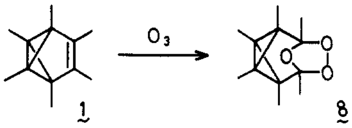


Compound 4 seemed to be a good precursor for the tetrahedrane. Photolysis of 4, however, gave *syn*- and *anti*-pentacyclo[$4.4.0.0^{2,4}.0^{3,5}.0^{7,10}$]decene compounds (5 and 6), and these reverted thermally to 4.[10] These results served to demonstrate the remarkable stability of the bicyclobutane moiety in this series of compounds. Warrenner et al. independently obtained 5 and 6 by the reaction of 1 with cyclobutadiene,[11] but their assignment of stereochemistry was contrary to ours, which is based on X-ray crystallography.[12]

The photocyclization of 4 shown in Scheme II suggested that the distance between C-7 and C-10 was very short. Further, cyclobutadiene was the only diene that added to 1 to give the syn adduct (5), indicating that the steric requirement of cyclobutadiene is very small. Therefore, if some bulky substituents were introduced at C-7 and C-10, the photocyclization might be suppressed and concerted cleavage to the tetrahedrane might occur.

Flash thermolysis of 4 gave 1,2-bis(trifluoromethyl)benzene and the dimer (7) of tetrakis(trifluoromethyl)cyclobutadiene.[10] This reaction as a concerted process is forbidden by the Woodward–Hoffmann rules. Presumably the biradical intermediate undergoes rearrangement to the cyclobutadiene, which dimerizes rapidly, as shown in Scheme III.

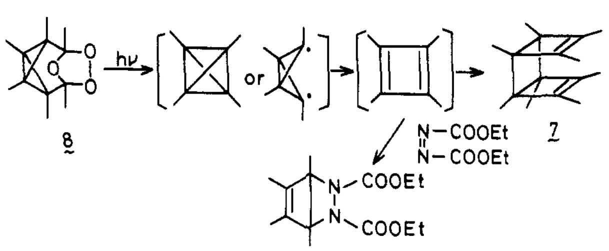
Route through the Ozonide of 1. Bubbling of ozone into a solution of 1 in pentane at −20 to −10 °C gave its ozonide (8), which was stable at room temperature[13] (eq 3). The marked stability of 8 is attributed to the Rf effect.



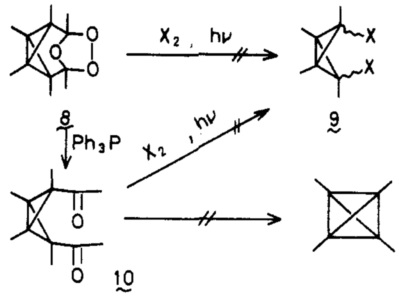
[3]

Irradiation with a high-pressure mercury lamp of the matrix formed by cooling the solution of 8 in 3-methylpentane at −196 °C produced a yellow coloration. This yellow color persisted at −196 °C after the light was turned off. As the matrix thawed, the yellow color disappeared and colorless crystals of 7 precipitated at once. We think that the yellow substance was the cyclobutadiene monomer. Actually, when this photolysis was carried out in the presence of diethyl azodicarboxylate, the cyclobutadiene was trapped as a 2,3-diazabicyclo[2.2.0]hexene derivative,[13] as shown in Scheme IV.

Scheme IV



Scheme V



Chapman reported in a lecture in 1976 that the tetrahedrane was observed on photolysis of 8 in an argon matrix at 8 K, but he has not published this work yet. Masamune[14] reported in 1977 that not the tetrahedrane but the cyclobutadiene monomer, recognized by its IR and UV spectra, was formed on photolysis of 8 in an argon matrix. It is not clear whether the tetrahedrane compound was generated during photolysis of 8. If Chapman's result was correct, the stabilizing effect of the trifluoromethyl groups was not large enough to enable the isolation of tetrahedrane. Masamune considers that 8 is not a good precursor for the tetrahedrane and that tetrakis(trifluoromethyl)tetrahedrane might be stable, if it were isolated.

In 1978, Maier[15] synthesized tetrakis(*tert*-butyl)tetrahedrane, which was surprisingly stable and showed a melting point of 135 °C. We feel that there is a chance that tetrakis(trifluoromethyl)tetrahedrane might be isolated, if a suitable precursor were utilized.

Next, we attempted to convert 8 into a dihalobicyclobutane derivative (9), directly or through the dicarbonyl compound (10), by the routes shown in Scheme V.

However, both attempts were unsuccessful. Attempted photoconversion of 10 to a tetrahedrane was also fruitless. While treatment of 8 with 1 mol of triphenylphosphine gave the dicarbonyl compound 10, treatment of 8 with 2 mol of triphenylphosphine or treatment of 10 with another mole of triphenylphosphine gave two valence bond isomers (11 and 12) of 2,3,4,5,6,7-hexakis(trifluoromethyl)oxepin.[16] The presumed mechanism of their formation is shown in Scheme VI. The postulated intermediate (13) apparently rearranges smoothly to 12. We tried photoisomerization of 12 to 13, but there was no apparent change at room temperature. We are now planning photoreaction at a low temperature to verify this mechanism. The photoreaction of 11 gave *E* and *Z* isomers of a

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[11] Warrener, R. N.; Nunn, E. E.; Paddon-Row, M. N. *Tetrahedron Lett.* **1975**, 2639.

[12] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Hanzawa, Y.; Honda, M.; Miyashita, W. *Tetrahedron Lett.* **1977**, 1795.

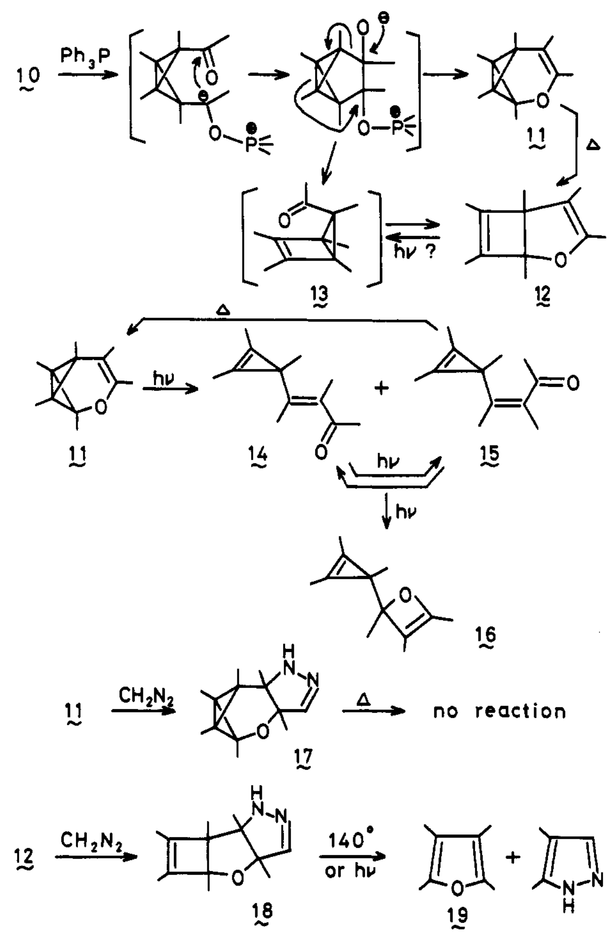
[13] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Honda, M.; Iitaka, Y. *Tetrahedron Lett.* **1975**, 3001.

[14] Masamune, S.; Machiguchi, R.; Aratani, M. *J. Am. Chem. Soc.* **1977**, *99*, 3524.

[15] Maier, G.; Pfriem, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 519.

[16] Kobayashi, Y.; Hanzawa, Y.; Nakanishi, Y. *Tetrahedron Lett.* **1977**, 3371.

Scheme VI



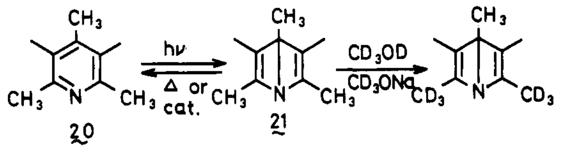
cyclopropenyl vinyl ketone (14 and 15). Compound 15 was thermally converted to 11 by a [2 + 2 + 2] mechanism, while 14 was thermally stable. Photoreaction of 14 or 15 gave a cyclopropenyloxetene (16).[17]

Reactions of 11 and 12 with diazomethane gave 1,3-dipolar cycloadducts 17 and 18, respectively. Thermolysis of 18 gave tetrakis(trifluoromethyl)furan,[18] which was independently synthesized by Lemal[19] and Chambers,[20] at nearly the same time. Although 11 thermally isomerized to 12, 17 was thermally stable. This result suggests that isomerization of 11 to 12 is not a simple rearrangement in the bicyclobutane moiety but that the double bond of the enol ether structure participates in this isomerization.

Valence Bond Isomers of Heteroaromatic Compounds

While many valence bond isomers of benzenes substituted with fluorine and/or fluoroalkyl groups have been reported, the chemistry of valence bond isomers of heterocyclic compounds is hardly known except for the valence bond isomers of diazines investigated mainly by Chambers and his colleagues[21] and that of pentakis(pentafluoroethyl)pyridine by Haszeldine.[22]

Scheme VII



Valence Bond Isomer of Pyridine. Our first aim was synthesis of pentakis(trifluoromethyl)pyridine and its valence bond isomer, but we could not obtain the pyridine itself. During the course of our research, Haszeldine reported the isolation of a Dewar-type isomer of pentakis(perfluoroethyl)pyridine and its unusual stability.[22] Then, we tried to synthesize valence bond isomers of pyridine of appropriate stability. Irradiation of 2,4,6-trimethyl-3,5-bis(trifluoromethyl)pyridine (20) gave a 1,4-bonded Dewar pyridine (21), which could be thermally isomerized back to 20[23] (see Scheme VII). Treatment of 21 with $NaOCD_3$ in CD_3OD caused deuterium exchange at the 2- and 6-methyl groups, but not at the 4-methyl group, while all the methyl groups of 20 underwent this exchange reaction. This suggests that push–pull electronic interaction between the methyl and trifluoromethyl groups may contribute to the stability of 21.[23]

Isomerization of 21 to 20 was catalyzed by Lewis acids and by some metal compounds, like rhodium chloride and iron carbonyls. Palladium(II) and platinum(II) salts formed isolable complexes with 21, which slowly isomerized to complexes of 20.[24] A planar tetragonal N (σ) structure for the mixed complex, $PdCl_2$·20·21, was established by X-ray analysis.[25]

Tetrakis(trifluoromethyl)(Dewar thiophene). Photoisomerization of substituted thiophenes had long been known. Some valence bond isomers have been postulated as intermediates, but none of them had been isolated or observed spectroscopically.

In 1970, we irradiated tetrakis(trifluoromethyl)thiophene (22) and isolated an isomer. Then, we noticed that Heicklen had isolated the same isomer and proposed first a Dewar structure (23).[26] but then a cyclopropenyl thioketone formula (24),[27] and finally the Dewar structure again on the basis of the ^{19}F NMR spectrum.[28] Independently, we examined the structure by ^{19}F and ^{13}C NMR. As only two kinds of CF_3 fluorines and carbons were observed, the Dewar-type structure 23 was confirmed.[29-31] Further, we carried out Diels–Alder reactions with furan derivatives and confirmed the structure of the adduct with tetra-

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[17] Kobayashi, Y.; Hanzawa, Y. Miyashita, W.; Kashiwagi, T.; Nakano, T.; Kumadaki, I. *J. Am. Chem. Soc.* **1979**, *101*, 6445.

[18] Kobayashi, Y.; Hanzawa, Y.; Nakanishi, Y.; Kashiwagi, T. *Tetrahedron Lett.* **1978**, 1019.

[19] Boriack, C. J.; Laganis, E. D.; Lemal D. M. *Tetrahedron Lett.* **1978**, 1015.

[20] Chambers, R. D.; Lindley, A.; Whittaker, G. *J. Chem. Soc., Chem. Commun.* **1978**, 475.

[21] E.g.: Chambers, R. D.; Maslakiewicz, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 1005 and references therein.

[22] Clifton, E. D.; Flowers, W. T.; Haszeldine, R. N.; Barlow, M. G.; Dingwall, J. G. *J. Chem. Soc., Chem. Commun.* **1969**, 1216.

[23] Kobayashi, Y.; Ohsawa, A.; Baba, M.; Sato, T.; Kumadaki, I. *Chem. Pharm. Bull.* **1976**, *24*, 2219.

[24] Kobayahsi, Y.; Ohsawa, A. *Chem. Pharm. Bull.* **1976**, *24*, 2225.

[25] Kobayashi, Y.; Ohsawa, A.; Iitaka, Y. *Tetrahedron Lett.* **1973**, 2643.

[26] Wiebe, H. A.; Braslavsky, S.; Heicklen, J. *Center for Air Environmental Studies Report*, **1970**, No. 164-70, p 1.

[27] Wu, E.; Heicklen, J. *J. Am. Chem. Soc.* **1971**, 93, 3432.

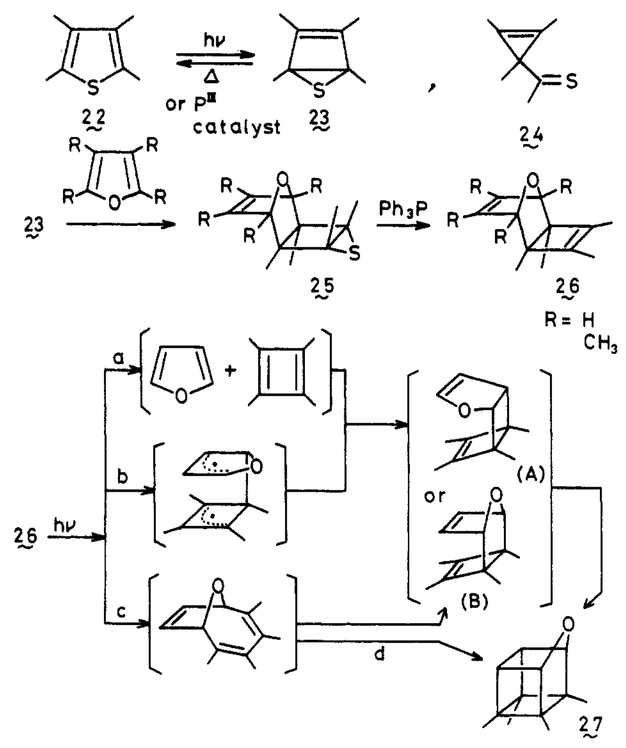
[28] Wiebe, H. A.; Braslavsky, S.; Heicklen, J. *Can. J. Chem.* **1972**, *50*, 2721.

[29] Kobayashi, Y.; Ohsawa, A.; Sekine, Y.; Kumadaki, I. 93rd Annual Meeting of Parmaceutical Society of Japan, Tokyo, **1973**. Abstracts, Part II, p 146.

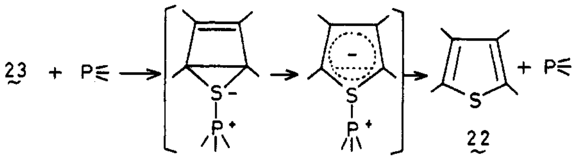
[30] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Tetrahedron Lett.* **1974**, 2841.

[31] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Mochizuki, H. *Chem. Pharm. Bull.* **1975**, *23*, 2773.

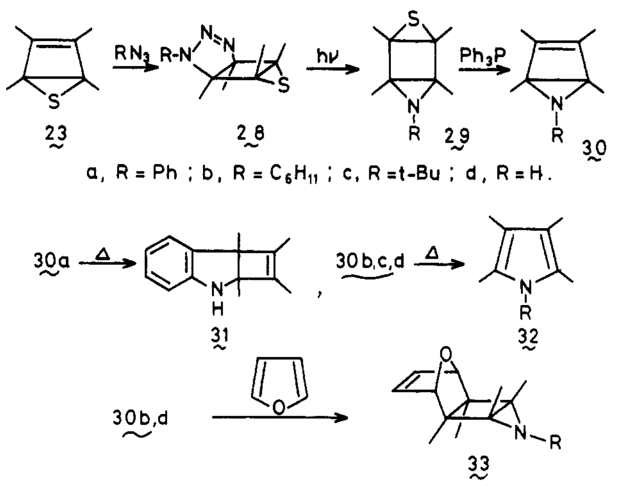
Scheme VIII



Scheme IX



Scheme X



methylfuran by X-ray analysis as the exo-anti structure **25**.[32] Compound **25** was smoothly desulfurized to tricyclic compound **26**. Irradiation of **26** with a low-pressure mercury lamp gave oxahomocubane compound (**27**).[30,31] This is a rare example in which an anti isomer gives a cage compound. Change of the configuration must have occurred before cyclization.

Possible mechanisms are shown in Scheme VIII. Route a is a photochemical [4 + 4] cycloreversion followed by thermal cycloaddition to the syn-intermediate A or B; route b is photochemical one-bond fission to a biradical followed by rotation and recombination to A or B; route c is a photochemical [2 + 2] ring opening followed by [2 + 2] recyclization to B; and in route d, the intermediate in route c cyclized directly to **27** by a [2 + 2 + 2] mechanism.

Isomerization of **23** to **22** was caused thermally ($t_{1/2}$ = 5.1 h at 160 °C). Surprisingly, trivalent phosphorus compounds did not abstract sulfur from **23**, but catalyzed the isomerization of **23** to **22**: trialkoxyphosphines and triphenylphosphine were good catalysts for this reaction, and diphenylchlorophosphine formed a crystalline complex with **23**, which was characterized by ^{19}F and ^{31}P NMR and which decomposed spontaneously to the phosphine and **22**. Phenyldichlorophosphine and phosphorus trichloride did not work at all. From these results, we gather that the lone-pair electrons play an important role in this reaction. We speculated that the mechanism of catalysis involves a 6π transition state, as shown in Scheme IX.[33,34]

Dewar Pyrroles from the Dewar Thiophene. As the Dewar thiophene **23** was found to be a good dienophile, we next tried the 1,3-dipolar reaction of **23** with azides. Adducts of type **28** were isolated in a very high yield with all the azides examined.[35–37] Especially surprising was the reaction with hydrogen azide, which was known to undergo the 1,3-dipolar cycloaddition only with active acetylenic compounds, but not with any olefinic compounds. This means that **23** is an extremely good dipolarophile.

The azide adducts **28** were photochemically denitrogenated to the valence bond isomers **29** of 1,4-thiazine, which were desulfurized with triphenylphosphine to Dewar pyrroles (**30**) (Scheme X). The *N*-phenyl compound **30a** underwent smooth rearrangement to cyclobutaindole (**31**) at room temperature via a Cope rearrangement type of mechanism. Other Dewar pyrroles (**30b–d**) isomerized to the corresponding usual pyrroles (**32b–d**) at higher temperature. Irradiation of *N*-phenylpyrrole (**32a**) gave **31** very slowly. This phenomenon seems reasonably explained by slow isomerization of **32a** to **30a**, which rapidly isomerizes to **31**. Irradiation of the *N*-cyclohexyl compound **32b** caused no observable change in ^{19}F NMR, while **30b** was photochemically isomerized to **32b**. Therefore, in the absence of an olefinic bond suitably disposed for Cope rearrangement, photoequilibrium between **32b** and **30b** tends toward the former compound. The Dewar pyrrole (**30b**) reacted with furan to give Diels–Alder adduct (**33**),[35,36,38] while butadiene and 2,3-dimethylbutadiene did not react. The reason why the latter diene did not

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[32] Kikutani, N.; Iitaka, Y.; Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Acta Crystallogr., Sect. B* 1975, *31*, 1478.

[33] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y. *Tetrahedron Lett.* 1975, 1639.

[34] After the submission of this paper, Lemal et al. proposed another structure for the intermediate complex at the Second Chemical Conference of the North American Continent, August 1980, Las Vegas, NV ("Abstracts of Papers"; American Chemical Society: Washington, DC, 1980). Their proposal was based on some P–F couplings. However, we think the couplings are too small to support the adduct formula they propose.

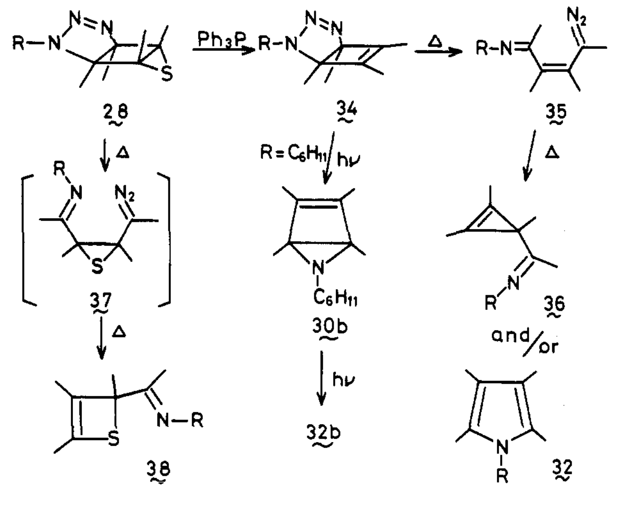
[35] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Ando, A. *J. Am. Chem. Soc.* 1977, *99*, 7350.

[36] Kobayashi, Y.; Ando, A.; Kumadaki, I. *J. Chem. Soc., Chem. Commun.* 1978, 509.

[37] Kobayashi, Y.; Ando, A.; Kawada, K.; Ohsawa, A.; Kumadaki, I. *J. Org. Chem.* 1980, *45*, 2962.

[38] Kobayashi, Y.; Ando, A.; Kawada, K.; Kumadaki, I. *J. Org. Chem.* 1980, *45*, 2966.

Scheme XI



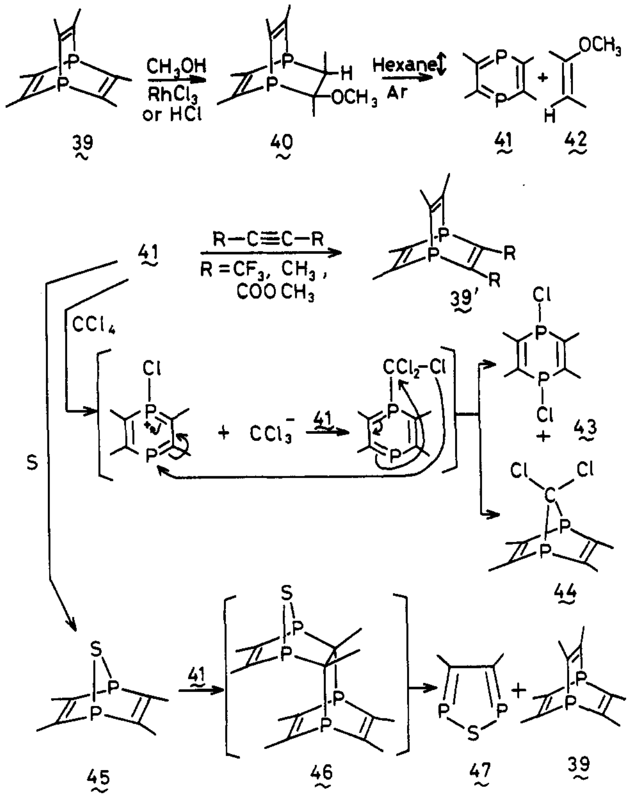
react is now being investigated.

When the order of denitrogenation and desulfurization was reversed, another feature of transformation was observed. Treatment of substances of type **28** with triphenylphosphine gave cyclobutatriazoles (**34**), which underwent thermal ring opening to diazoimine compounds (**35**) (Scheme XI). The latter gave cyclopropenylimine (**36**) and/or pyrrole compounds (**32**) on thermolysis, depending on the substituent on the nitrogen: **35a** → **32a**, **35b** → **36b** + **32b** (3:1), **35c** → **36c**. As treatment of **36b** under the same conditions did not give **32b**, **36b** was not an intermediate enroute to **32b**. Probably, **32b** was formed directly from **35b**.[39] Irradiation of **34b** with a high-pressure mercury lamp gave **30b**, which was converted to **32b** by further irradiation.

Heating the dipolar adducts **28** converted them into thiete derivatives (**38**). In the case of the *N*-phenyl isomer (**28a**), diazothiirane **37a** was isolated as an intermediate. These results show that thermolysis of dihydrotriazole compounds (**28** and **34**) causes retro-1,3-dipolar type ring opening ([4 + 2] reaction), whereas their photolysis gave denitrogenated products ([2 + 2] reaction). These results are also shown in Scheme XI.

1,4-Diphosphorin and Other New Ring Systems. Phosphorins (phosphabenzenes) have been synthesized independently by Märkl[40] and by Ashe,[41] but no diphosphorin had been synthesized in spite of many efforts. We expected that the stabilizing effect of a trifluoromethyl group might facilitate isolation of a diphosphorin. We chose diphosphabarrelene (**39**), 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene, as a starting material. For the purpose of removing one $CF_3C{\equiv}CCF_3$ unit from **39**, its conversion to a dihydro form seemed to be favorable, since dihydrobarrelenes are known to be prone toward retrocycloaddition to benzene and olefins. The methanol adduct **40** was easily obtained by treatment of **39** with rhodium chloride in methanol (Scheme XII). Compound **40** did not show the parent peak in its mass spectrum, but large fragment peaks were observed at *m*/*z* 386 [corresponding to tetrakis(trifluoromethyl)-1,4-diphosphorin (**41**)] and 194 [$CF_3HC{=}C(OCH_3)CF_3$]. Accordingly, a solution of **40** in hexane was heated

Scheme XII



under a reflux condenser cooled with tap water in a stream of dry and perfectly deoxygenated argon. The exit gas was passed through a trap cooled in dry ice/acetone. The course of reaction was followed by the amount of olefin **42** collected in the trap. When no more olefin was observed by ^{19}F NMR, the content of the reaction flask was analyzed in an atmosphere of argon. Compound **41** was recognized by a doublet in its ^{19}F NMR spectrum, one multiplet in the ^{31}P NMR, and λ_{max} 282 nm ($\epsilon > 5000$). These data show that **41** has a symmetrical planar structure of some aromatic character. However, **41** is very sensitive to oxygen, and accurate measurement of the intensity of its UV spectrum was very difficult, since a trace of oxygen decomposed **41** slowly in low concentration. The structure of **41** is supported by the reactions shown in Scheme XII.[42,43]

Compound **41** reacted as a diene with acetylenic compounds to give diphosphabarrelenes of type **39′**. Inasmuch as phosphorin reacted as a diene with acetylenic compounds, this reaction supports the assignment of structure **41**.[42,43]

Treatment of **41** with carbon tetrachloride gave a new diphosphanorbornadiene derivative (**44**).[44] Compound **43** was also formed, as confirmed by ^{19}F NMR. The mechanism for the formation of both products was speculated to be as shown in Scheme XII. It is suggested that the phosphorus atoms of **41** have the character of trivalent phosphorus, while those of **39** do not. This difference between **39** and **41** was more clearly shown in the reaction of **41** with sulfur.

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[39] Kobayashi, Y.; Ando, A.; Kawada, K.; Kumadaki, I. *J. Org. Chem.* **1980**, *45*, 2968.

[40] Märkl, G. *Angew. Chem.* **1966**, *78*, 907.

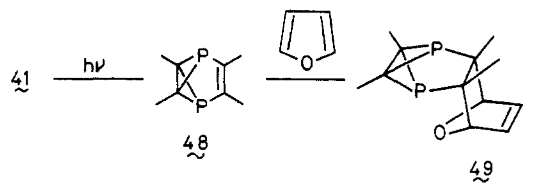
[41] Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 3293.

[42] Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Hamana, H. *Tetrahedron Lett.* **1976**, 3715.

[43] Kobayashi, Y.; Hamana, H.; Fujino, S.; Ohsawa, A.; Kumadaki, I. *J. Am. Chem. Soc.* **1979**, *102*, 252.

[44] Kobayashi, Y.; Kumadaki, I.; Hamana, H.; Fujino, S. *Tetrahedron Lett.* **1977**, 3057.

Scheme XIII



Treatment of **41** with an excess of sulfur gave the thiadiphosphanorbornadiene (**45**), while 0.5 equiv of sulfur gave thiadiphosphole (**47**) and **39**. Thus, sulfur was trapped by **41** to give **45** which has the character of a dienophile and reacted with an excess of **41** to give adduct **46**. This adduct (**46**) has a partial dihydronorbornadiene structure and seems to have been cleaved to **47** and **39** (Scheme XII).

Finally, we show in Scheme XIII the first example of a benzvalene analogue containing a heteroatom in the ring. Irradiation of **41** with a high-pressure mercury lamp gave diphosphabenzvalene (**48**),[45] which showed the presence of two kinds of trifluoromethyl in its ^{19}F NMR spectrum (one a doublet, the other a triplet, by P–F coupling) and a single kind of phosphorus in its ^{31}P NMR spectrum. Compound **48** reacted with furan to give an adduct (**49**), just as benzvalene (**1**) did.

A curious feature of these phoshorus compounds is that planar trivalent phosphorus compounds (**41**, **43**, and **47**) are very sensitive to air, while bicyclic cage compounds (**39**, **44**, **45**, **48**, **49**) are stable to air. This offers an interesting problem to theoretical chemists.

Concluding Remarks

In this Account, we have shown many examples in which trifluoromethyl groups stabilize otherwise unstable ring systems. This stabilization may be due in part to steric effects. However, this cannot be the sole factor responsible, as mentioned before. Some changes in hybridization on carbon atoms due to the high electronegativity of fluorine atoms, and some p–π repulsion might make important contributions in some cases. We are now planning to examine steric effects by means of force-field calculations, and electronic effects by MO calculations.[46]

(45) Kobayashi, Y.; Fujino, S., Hamana, H.; Kumadaki, I.; Hanzawa, Y. *J. Am. Chem. Soc.* 1977, *99*, 8511.

(46) After the submission of this paper, Greenberg et al. reported theoretical calculation of the perfluoroalkyl effect. (Greenberg, A.; Liebman, J. F.; Van Vechten, D. *Tetrahedron* **1980**, *36*, 1161). According to their calculations, a trifluoromethyl group does not stabilize strained compounds. They were concerned with energy differences between unsubstituted and trifluoromethylated compounds. We use the word "stabilized" when a strained ring system is formed from the parent aromatic compound. Our concern is with the small energy difference between the strained ring system and the aromatic compound with trifluoromethyl groups and the fast formation and slow decomposition of strained ring systems with trifluoromethyl groups. Slow decomposition may be partly due to the "siphoning" of vibrational energy into perfluoroalkyl groups, as mentioned by Greenberg et al.

Aspects of Longifolene Chemistry. An Example of Another Facet of Natural Products Chemistry

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Received August 20, 1980

There are several facets of natural product chemistry: structure elucidation, synthesis, biostudies, and transformations. Classically, structure elucidation was the prime motivation for the study of a natural product, whether biologically active or just an academic curiosity. Degradation, transformations, synthesis—all formed an integral part of this exercise. However, with the introduction of spectroscopic techniques, the role of chemical reactions in structure determination has become minimal. Increasingly, complex organic structures are being elucidated by X-ray crystallography, a technique which essentially bypasses the organic chemist! These advances constitute a watershed in the development of chemistry of natural products and have enabled chemists to direct efforts to aspects of natural products chemistry considered unassailable until recently. On the other hand, the classical approach involving chemical transformations had, in the past, generated a fund of interesting and unexpected results, often of fundamental importance. This is because many complex natural products have such built-in stereoelectronic features that their chemical transformations, not too infrequently, led to unanticipated results.[1] It is suggested that chemical transformations of easily available, novel, complex organic molecules deserve to be investigated so that the excitement of the unexpected is not completely lost!

Longifolene, $C_{15}H_{24}$, is a tricyclic olefin and occurs to the extent of 5–10% in the Indian turpentine oil, which is produced commercially from the oleoresin of Himalayan pine, *Pinus longifolia* Roxb. Its structure (**1**) was established[2] in 1953, but still over 25-years later, it continues to attract attention as a novel substrate for

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(1) Viewed with hindsight, such results offer little difficulty in rationalization!

(2) R. H. Moffett and D. Rogers, *Chem. Ind.* (*London*), 916 (1953); P. Naffa and G. Ourisson, *ibid.*, 917 (1953).

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