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REACTIONS OF TETRAKIS(TRIFLUOROMETHYL)DEWAR THIOPHENE

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Introduction

Since it is well known that some aromatic compounds with trifluoromethyl groups give fairly stable valence-bond isomers on photolysis[1], we examined the photolysis of tetrakis(trifluoromethyl)thiophene (I). During the course of our work, Heicklen and others reported that the photolysis of I at 2139 Å or 2537 Å with Hg sensitization gave the isomer of I. At first, they proposed the Dewar type[2a] (II), next cyclopropenylthioketone type[2b] (III), and again the Dewar type[2c] for the structure of this isomer. Thus, their assignment of the structure did not seem decisive. We found that the photolysis of I at 2537 Å in gas phase without any sensitizer gave an isomer in a most satisfactory yield and determined it to be the Dewar type (II), based on the analysis of ^{19}F- and ^{13}C-NMR and IR spectra[3] (Chart 1). Its structure was further confirmed by X-ray analysis of the Diels-Alder adduct of I with tetramethylfuran[4]. It was found that II reverted to I thermally or by the catalysis of phosphorous compounds. The olefinic bond of II is highly strained and substituted with electronegative trifluoromethyl group. Thus, II reacted as a good dienophile and dipolarophile. Furthermore, the Diels-Alder adducts of II with furans were derived to oxahomocubane compounds. From the 1,3-dipolar cycloadducts, compounds of a new and interesting ring system, Dewar pyrrole, were obtained.

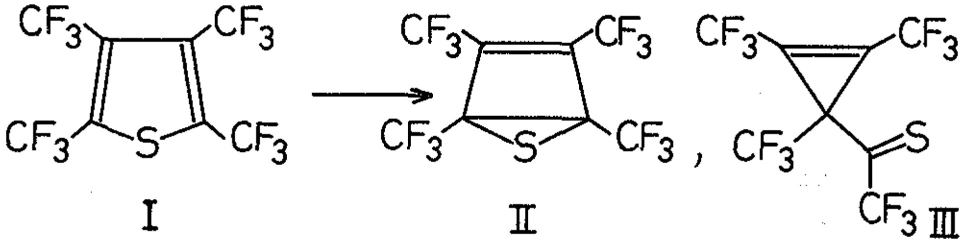


Chart 1

Isomerization of II to I[5]

The reversion reaction of II to I is a forbidden reaction according to Woodward-Hoffmann rule. Therefore, II is rather stable in thermolysis; its half-life in benzene at 160° was 5.1 h. This reversion took place smoothly at room temperature in the presence of triphenylphosphine, where formation of an intermediate was not observed. When diphenylchlorophosphine was used as a catalyst, the reaction became slower than in the presence of triphenylphosphine, and when the reaction was carried out in a high concentration, an unstable complex (IV) was isolated. The structure of IV was determined by ^{19}F- and ^{31}P-NMR and IR spectra. The complex (IV) was spontaneously decomposed to I and diphenylchlorophosphine. Phenyldichlorophosphine and phosphorous trichloride were ineffective as a catalyst, which means that lone-pair electrons on the phosphorus atom take part in this reversion. Therefore, the reaction path was assumed as shown in

Chart 2; the Dewar thiophene becomes 6π-system (V) by the contribution of lone-pair electrons of the phosphorus atom. The fact that pentavalent phosphorus compounds show no catalytic effect supports this mechanism.

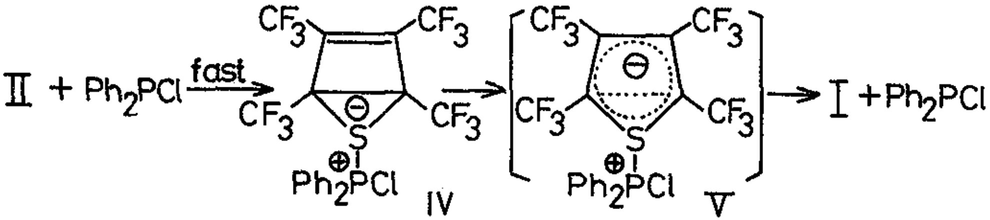


Chart 2

When I was dissolved in polar aprotic solvents such as dimethyl sulfoxide, the dimer (VI) precipitated immediately. Since VI shows the absorption due to the cyclobutene double bond at 1700 cm^{-1}, this dimerization must have occurred through the thiirane ring[3] (Chart 3).

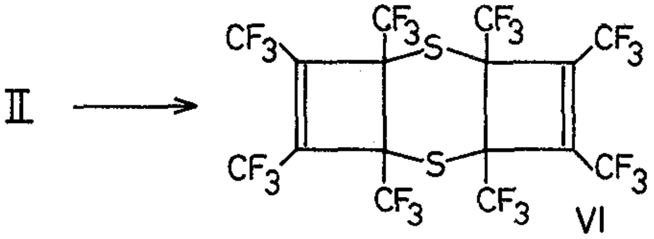
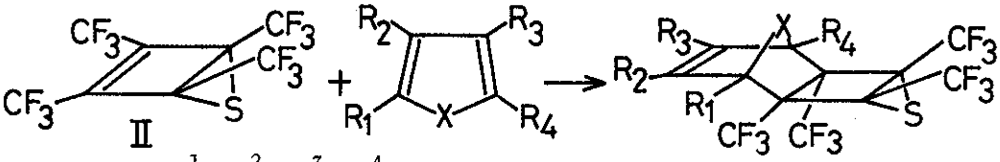


Chart 3

Diels-Alder Reaction and Transformation of the Adducts[3]

Compound (II) was found to be a good dienophile in the Diels-Alder reaction with acyclic and cyclic dienes. Its results are summarized in Table I.

The structure of VIIb was determined by X-ray analysis[4], and the difference in the reactivity among the dienes can reasonably be explained by approach from the exo-side in the transition state, similar to VIIb.



- X -	R^1	R^2	R^3	R^4	temp.	time	yield
-H,H-	H	H	H	H	r.t.	6 day	70%
-H,H-	CH_3	H	H	H	r.t.	7 day	16%
-H,H-	H	CH_3	H	H	r.t.	3 day	63%
-H,H-	H	CH_3	CH_3	H	r.t.	1 day	78%
-H,H-	CH_3	H	H	CH_3	80°C	5 day	no reaction
-O-	H	H	H	H	r.t.	30 min	49% (VIIa)
-O-	CH_3	CH_3	CH_3	CH_3	r.t.	1 day	66% (VIIb)
-O-	CH_3	CF_3	CF_3	CH_3	80°C	5 day	no reaction
-NH-	H	H	H	H	r.t.	30 min	70%
$-NCH_3-$	H	H	H	H	80°C	5 day	no reaction
$-CH_2-$	H	H	H	H	r.t.	25 min	80%
$-CH_2CH_2-$	H	H	H	H	r.t.	7 day	15%*

*

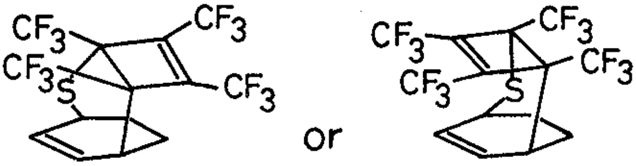


Table I Diels-Alder Reaction of II with Dienes

The adducts (VIIa and VIIb) were desulfurized with triphenylphosphine to give 9-oxatricyclo[4.2.1.$0^{2,5}$]nonadiene compounds (VIII), which were converted to oxahomocubane compounds (IX) on photolysis in acetonitrile with a low-pressure mercury lamp. This cyclization reaction might have followed one of the two paths shown in Chart 4, since the radical mechanism could be ruled out by the fact that this reaction was not affected by a radical scavenger, 1,3-pentadiene.

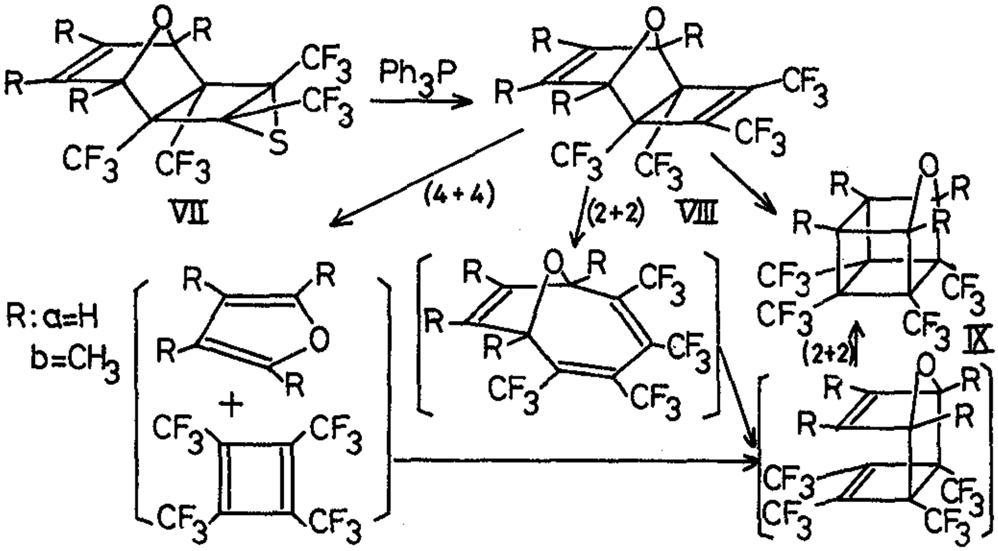


Chart 4

1,3-Dipolar Cycloaddition Reaction with Azides[6]

The compound (II) was found to react with azides as a good 1,3-dipolarophile to give 3-thia-6,7,8-triazatricyclo[3.3.0.-$0^{2,4}$]octene compounds (X), which lost the nitrogen molecule on photolysis in the formation of novel valence bond isomers (XI) of thiazine. The compound XI were desulfurized to compounds (XII) of quite an interesting ring system, Dewar pyrrole. The compound (XIIa) spontaneously isomerized to cyclobutaindole compound (XIII). N-Cyclohexyl compound (XIIb) reacted with furan to give 10-oxa-4-azatetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]decene compound (XIV) (Chart 5).

Conclusion

The olefinic bond of the Dewar thiophene (II) was found to be a good 2π-component in (4π + 2π)-cyclization reaction. The sulfur atom could be removed later. Therefore, II is very useful in the synthesis of compounds having a trifluoromethylated cyclobutene ring.

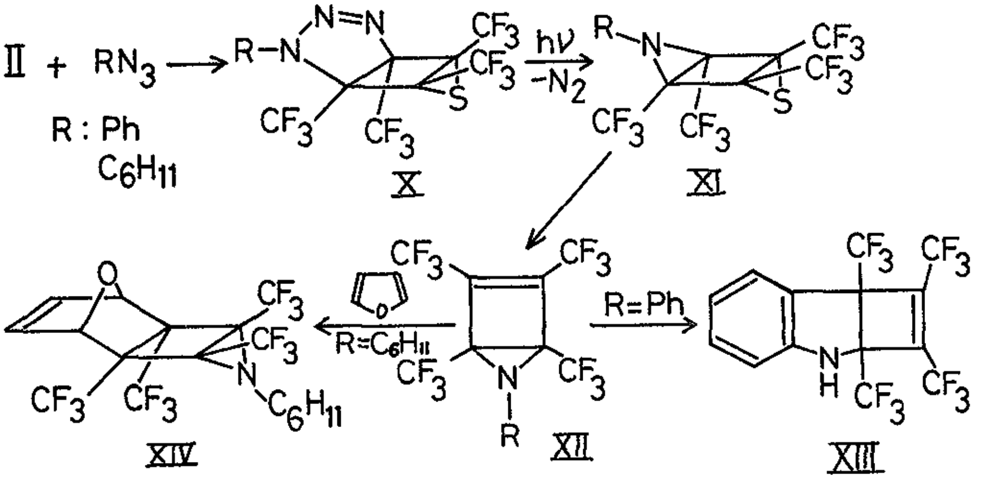


Chart 5

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6. Submitted to J.Am.Chem.Soc. for publication. The details will be presented at the 26th International Congress of Pure and Applied Chemistry, September 1977.