hydroxide in 5 mL of ethanol. The compound dissolved. The ethanol was evaporated, the residue was dissolved in water, and the free acid was precipitated by adding hydrochloric acid. The acid was filtered off and recrystallized from acetone to give 1.80 g (80%) of 2-hydroxy-3-(2,3,4,5-tetrachlorophenyl)acrylic acid in two crops: mp 209.5–210 °C; NMR (DMF-d_7) 6.69 (s, removed by D_2O, CH), 8.40 (s, aromatic H), 10.30 (OH + COOH).

Anal. Calcd for $C_9H_4Cl_4O_3$: C, 35.80; H, 1.34; Cl, 46.97. Found: C, 36.12; H, 1.28; Cl, 46.65.

Reaction of Tetrachlorothiophene Dioxide with α-Angelica Lactone. α-Angelica lactone[8] (1.18 g, 0.012 mol) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated on a steam bath for 1.5 h. The reaction product solidified and was recrystallized from acetone to give 1.80 g (62%) of (2,3,4,5-tetrachloro-6-methylphenyl)acetic acid (**13**) in two crops: mp 245.5–247 °C; NMR [$(CD_3)_2SO$] 2.43 (s, CH_3), 3.93 (s, CH_2), 11.5 (br, low peak, OH); IR 3333 (OH), 1695 cm^{-1} (C=O); mass spectrum, *m/z* 285.9091 (parent), 250.9417 (–Cl), 240.9067 (–COOH).

Anal. Calcd for $C_9H_6Cl_4O_2$: C, 37.53; H, 2.10; Cl, 49.24. Found: C, 37.46; H, 2.16; Cl, 48.69.

Synthesis of 10 from 2,5-Dimethoxy-2,5-dihydrofuran. 2,5-Dimethoxy-2,5-dihydrofuran[8] (1.95 g, 0.015 mol, 1:2 cis-trans mixture) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were warmed together. The temperature rose to 120 °C and was moderated by cooling. After the reaction subsided, excess 2,5-dimethoxy-2,5-dihydrofuran was removed under vacuum. The residue was rinsed with cold methanol to give 1.62 g (51%) of product. Recrystallization from hexane left 1.45 g (45%) of methyl (2,3,4,5-tetrachlorophenyl)acetate (**10**, Table I), mp 88–89 °C.

Addition of Tetrachlorothiophene Dioxide to 2-Vinylfuran. 2-Vinylfuran[9] (4 mL), 10 mL of 1,2-dichloroethane, and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide were warmed in a flask with a reflux condenser and then cooled to moderate the vigorous reaction. The mixture was heated on a steam bath for 1 h after the reaction subsided. Distillation gave 3.65 g, bp 92–100 °C (0.4 mm), and 2.15 g of residue. The distillate was recrystallized from absolute ethanol to give 3.2 g (56%) of 2-(2,3,4,5-tetrachloro-2,4-cyclohexadienyl)furan (**14**): mp 67–68.2 °C; NMR ($CDCl_3$) 3.1 (m, CH_2), 3.97 (dd, CH of cyclohexadiene ring), 6.23 (m, 3-H and 4-H), 7.35 (m, 5-H).

Anal. Calcd for $C_{10}H_6Cl_4O$: C, 42.30; H, 2.13; Cl, 49.94. Found: C, 42.52; H, 2.34; Cl, 49.67.

Synthesis of 15. Tetrachlorothiophene dioxide (2.54 g, 0.01 mol), 10 mL of 1,2-dichloroethane, and 2.84 g (0.01 mol) of **14** were heated on a steam bath under reflux for 1 h. The solvent was removed and the residue was recrystallized from CCl_4 to give 3.18 g (69%) of **15**: mp 128–129 °C; NMR ($CDCl_3$) 3.12–3.72 (ABC, CH_2 + CH of cyclohexadiene ring), 4.07 (AB, CH_2CO), 7.27 (aromatic H); IR 3077 (=CH), 2933 (CH), 1715 (C=O), 1600, 1527 cm^{-1} (C=C).

Anal. Calcd for $C_{14}H_6Cl_8O$: C, 35.49; H, 1.28; Cl, 59.86. Found: C, 35.69; H, 1.52; Cl, 59.62.

Acknowledgment. I am indebted to F. A. Blissick for technical assistance and to E. W. Matthews for IR spectral interpretations.

Registry No. **1**, 72541-70-9; **2**, 72541-71-0; **3**, 72541-72-1; **4**, 72541-73-2; **5**, 72541-74-3; **6**, 72541-75-4; **7**, 72541-76-5; **8**, 72541-77-6; **9**, 72541-78-7; **10**, 72541-79-8; **11**, 72541-80-1; **12**, 72541-81-2; **13**, 72541-82-3; **14**, 72541-83-4; **15**, 72541-84-5; 3,4-dichlorothiophene dioxide, 52819-14-4; furan, 110-00-9; (2,3,4,5-tetrachlorophenyl)acetaldehyde, 72541-85-6; 2-hydroxy-3-(2,3,4,5-tetrachlorophenyl)acrylic acid, 72541-86-7; *cis*-2,5-dimethoxy-2,5-dihydrofuran, 5143-07-7; *trans*-2,5-dimethoxy-2,5-dihydrofuran, 5143-08-8; 2-vinylfuran, 1487-18-9; 2-methylfuran, 534-22-5; 2-butylfuran, 4466-24-4; 2,5-dimethylfuran, 625-86-5; 2-(acetoxymethyl)furan, 623-17-6; 2-(acetamidomethyl)furan, 5663-62-7; 2-(carbomethoxy)furan, 611-13-2; 2-acetylfuran, 1192-62-7; 2-methoxyfuran, 25414-22-6; tetrachlorothiophene dioxide, 72448-17-0; tetrabromothiophene dioxide, 72524-90-4; 2,5-dichlorothiophene dioxide, 72541-87-8; 2-angelica lactone, 591-12-8.

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[8] Aldrich Chemical Co., Milwaukee, WI.

[9] Polysciences, Inc., Warrington, PA.

Preparation and Selected Reactions of 2,3-Bis(bromomethyl)-1,3-butadiene[1]

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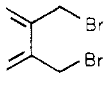
Received May 19, 1979

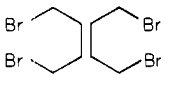
2,3-Bis(bromomethyl)-1,3-butadiene (**1**) was prepared by zinc-induced debromination of 1,4-dibromo-2,3-bis(bromomethyl)-2-butene (**2**). The versatility of **1** as a synthetic intermediate was demonstrated through consecutive use of its allylic bromides and conjugated diene functions, with eventual further modification of the primary reaction products. Coupling of **1** with vinylmagnesium chloride or ethynylmagnesium bromide gave highly unsaturated hydrocarbons (**8–11**). Reaction of **1** with nucleophiles such as sodium methoxide, sodium azide, sodium acetate, or potassium cyanide gave symmetrically disubstituted 1,3-butadienes (**12a–d**) which could in some cases be modified at the level of the substituent into other analogous dienes (**12e–f**). Five-membered heterocycles with exocyclic cis-fixed dienes, namely, the thiolane **13**, oxolane **14**, and pyrrolidines **15a–e** were obtained from **1** by reaction with sodium sulfide, with potassium hydroxide, or with secondary amines, respectively. Two of the pyrrolidines (**15a,c**) were photolytically cyclized into the corresponding 3-azabicyclo[3.2.0]heptene derivatives (**24a,b**). Dimethylenehexahydropyridazine derivatives (**28, 29**) were obtained from **1** by reaction with dimethyl azodicarboxylate and subsequent elimination of bromine. These unstable compounds could be stabilized as diene–iron tricarbonyl complexes (**31–34**). Carbocyclic systems were obtained from **1** by various Diels–Alder additions, such as the addition of dimethyl acetylenedicarboxylate which was followed by debromination and addition of a second molecule of the acetylenic ester to give a tetrahydronaphthalene derivative (**35** → **36** → **37**). Reaction of **1** with diiron nonacarbonyl produced three binuclear π complexes: the known 2,2′-bis(π-allyl) complex (**38**) and two isomeric trimethylenemethane-type complexes (**39, 40**) deriving from dimerization of **1**. The structure of the latter was proven by isomerization into bis(diene) complexes (**41, 42**) and oxidation to known hydrocarbons.

During the last few years we have been exploring the chemistry of the title compound, 2,3-bis(bromomethyl)-1,3-butadiene (**1**), a versatile reactive synthetic intermediate which was readily available by a zinc-induced debromination of 1,4-dibromo-2,3-bis(bromomethyl)-2-butene (**2**).[2-4] The versatility of **1** derives from its being both a 1,4 double allylic dibromide, active in displacement reactions, and a 1,3-diene, active in cycloadditions. Furthermore, the primary reaction products obtained by any of these routes conserve the feature of either a 1,3-diene or a 1,4-dibromo-2-ene derivative and may thus be further used in synthetic transformations, such as cycloaddition, photocyclizations, or elimination of bromine to regenerate a diene system.

We wish to present here a report on work carried out along these lines and to include a detailed description of the preparation of **1**.



1



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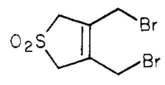


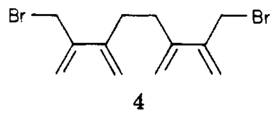
3

Debromination of Tetrabromide 2. Dibromide **1** has been prepared previously by the thermal elimination of sulfur dioxide from 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-dioxide (**3**).[5] It was obtained as an unstable solid and was used in some Diels–Alder additions.[5] The zinc-induced debromination of **2** provides dibromide **1** in its relatively stable solubilized form. Further reactions of **1** in a variety of solvents or at high temperatures may then proceed without noticeable polymerization.

Tetrabromide **2** is readily produced from 2,3-dimethyl-1,3-butadiene,[6] or, alternatively, from the hexane or hexene isomers possessing the same carbon skeleton[7] and also from pinacolyl alcohol.[8] Its debromination with zinc–copper couple[9] could be realized in a variety of solvents or solvent mixtures, with best results being obtained in ether with added hexamethylphosphoramide (HMPT). Under these conditions no tetrabromide remained unreacted and **1** was repeatedly obtained in 85–88% yield and in a purity of over 90%, which was satisfactory for most subsequent uses. Further purification could, however, be achieved by crystallization from pentane. The yield of colorless, pure, recrystallized **1** is 70–73%. A recently reported,[10] similar debromination method used very large relative amounts of activated tin and needed long reaction times.

Solid **1** polymerizes quite rapidly into a highly insoluble, probably cross-linked polymer. The yield and quality of the material is therefore best determined on a measured aliquot of the total solution.

The major impurity of crude **1** is the coupling product, 2,7-bis(bromomethyl)-3,6-dimethylene-1,7-octadiene (**4**), which shows in the ^{1}H NMR spectrum of the crude reaction product as an extra peak at δ 2.4. It could be isolated from the mother liquors of crystallization of **1** as the disulfone **5a** (n = 2) through reaction with sodium *p*-toluenesulfinate. Other products deriving from **4** could sometimes be isolated from other reactions of crude **1**.



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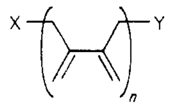
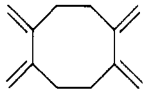
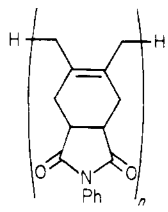


5a, X = Y = $CH_3C_6H_4SO_2$
b, X = Y = H
c, X = Br; Y = H
d, X = Y = Br
e, X = $CH_3C_6H_4SO_2$; Y = H
f, X = $CH_3C_6H_4SO_2$; Y = Br



6

Compounds of type **5b–d**, $n \geq 2$, of which **4** is a particular case, are produced when the zinc-induced debromination of **2**, or of **1**, is carried out in DMF as a solvent. In this case an exothermic reaction ensues, and after a reaction time of 20 h a multicomponent mixture of products **5b** is obtained in over 90% yield, together with a 2–5% yield of 1,2,5,6-tetramethylenecyclooctane (**6**). The lower **5b** members were separated by column chromatography and characterized through their spectral properties and through adducts **7** (n = 2, 3) with *N*-phenylmaleimide.



7

Tetraene **6**[11] was separated from an intimate mixture with **5b** (n = 2) by preparative GC and was likewise characterized. No attempt was made to separate compounds **5b** with $n > 4$, and they were eluted from the column, with ether, in one batch. Comparison of the ^{1}H NMR spectrum of the initial mixture with the spectra of the isolated products and of the ether fraction showed that all of these materials were of similar structures. They all showed singlets at δ 1.9 (olefinic methyls), 2.4 (aliphatic methylenes), and 5.0, 5.1 (methenes). The integration ratios of these signals, as well as the molecular weights of adducts **7**, gave the values of n of the isolated products. Polyenes **5a**, with $n > 13$, have been previously obtained through allene polymerization, using a homogeneous palladium catalyst.[12]

When the debromination of **1** in DMF was stopped after 2 h, products **5c** and **5d** were obtained. Some of the lower members could be separated by chromatography and characterized through their spectral properties and through the solid sulfones **5a** or **5e**, derived from them by reaction with sodium *p*-toluenesulfinate in HMPT.

Preliminary experiments only were carried out as mechanistic probes of the debromination reaction in DMF. Thus, quenching the reaction with D_2O did not produce terminally deuterated **5b** products. However, when the debromination was carried out in a 4:1 mixture of ether and deuterium oxide, **5b** products with X = Y = D were produced as evidenced by the mass spectrum of adduct **7** obtained from the isolated lower member. The reaction

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(1) Taken in part from Sadeh, S. Ph.D. Thesis, The Weizmann Institute, 1977.

(2) Gaoni, Y. *Tetrahedron Lett.* **1973**, 2361–4.

(3) Sadeh, S.; Gaoni, Y. *Tetrahedron Lett.* **1973**, 2365–8.

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(5) Butler, G. B.; Ottenbrite, R. M. *Tetrahedron Lett.* **1967**, 4873–6.

(6) Cope, A. C.; Kagan, F. *J. Am. Chem. Soc.* **1958**, *80*, 5499–502.

(7) Stetter, H.; Tresper, E. *Chem. Ber.* **1971**, *104*, 71–4.

(8) LeQuesne, P. W.; Reynolds, M. A.; Beda, S. E. *J. Org. Chem.* **1975**, *40*, 142–3.

(9) For a review on the formation of conjugated dienes from halogenated compounds by dehalogenation with metals, see Brachel, H.; Bahr, U. "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1970; Vol. 5/1C, pp 155–61.

(10) Dowd, P.; Marwaha, L. K. *J. Org. Chem.* **1976**, *41*, 4035–6.

(11) (a) Borden, W. T.; Sharpe, L.; Reich, I. L. *J. Chem. Soc. D* **1970**, 461–2. (b)Borden, W. T.; Reich, I. L.; Sharpe, L. A.; Weinberg, R. B.; Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2438–42. (c) Diversi, P.; Ingrosso, G.; Immirzi, A.; Porzio, W.; Zocchi, M. *J. Organomet. Chem.* **1977**, *125*, 253–71.

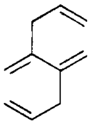
(12) Shier, G. D. *J. Organomet. Chem.* **1967**, *10*, P15–P17.

may thus involve homolytic cleavage of carbon–bromine bonds and formation of a monoradical derived from **1** which may couple to a dimer, **4**, and then further grow at the termini through a similar process or stop growing by abstraction of protons from the solvent or by cyclization to **6**.

The chemistry of **1** was studied by us both in an exploratory way, endeavoring to show its many-sided reactivity, and in a directed way, aiming at predetermined goals. The latter approach was mainly related to the problem of the 2,2′-bis(allyl) diradical,[13] of which **1** was considered to be a direct or an indirect precursor. An account of both approaches now follows.

Hydrocarbons. Dibromide **1** may be used in the preparation of hydrocarbons through coupling with Grignard reagents. Two such reactions, leading to highly unsaturated hydrocarbons, have been realized.

Reaction of **1** with vinylmagnesium chloride[14] produced 4,5-dimethylene-1,7-octadiene (**8**) in 40% yield, accompanied by 4,5,8,9-tetramethylene-1,11-dodecadiene (**9**; 10%). The two polyenes were separated by distillation and characterized through their spectral properties and analytical data and through their respective mono and bis adducts with *N*-phenylmaleimide. Tetraene **8** was found to be a quite stable compound, even in the free state.[15] Hexaene **9** could have been formed from dibromide **4** present in **1**, but in view of the large proportion obtained even from recrystallized **1**, it is believed to derive from a coupling reaction, induced by the Grignard reagent. It was found to be less stable a compound than **8**, polymerizing quite readily in the free state.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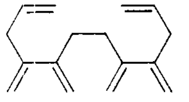
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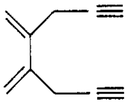
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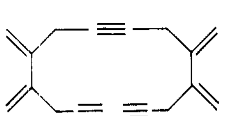
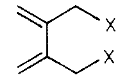

11

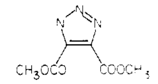
Reaction of **1** with ethynylmagnesium bromide[16,17] produced 4,5-dimethylene-1,7-octadiyne (**10**) and 4,5,10,11-tetramethylene-1,7,13-tetradecatriyne (**11**) in 45 and 9% yield, respectively. This reaction has been carried out only once and the products were then separated by chromatography. It is believed that if the reaction is carried out on a larger scale, a separation of **10** and **11** by direct distillation of the reaction mixture would be possible, as previously described,[16] and the yields would be improved.

The structures of **10** and **11** are based on their spectral and analytical data and on the preparation of an adduct of **10** with *N*-phenylmaleimide. Both **10** and **11** might be useful in oxidative coupling reactions leading to unsaturated macrocyclic compounds.

Symmetrically Substituted 1,3-Butadienes.[2] Disubstitution of **1** with nucleophiles such as sodium methoxide, sodium azide, sodium acetate, and potassium cyanide was found to proceed readily, with production of dienes **12a–d**, respectively, in good yields. Two of these, the bis(azidomethyl) derivatives **12b** and the bis(acetoxymethyl) derivative **12c**,[18] could be further reacted at the level of the substituent to give new, or known, dienes (**12e–h**). Thus, reduction of **12b** with lithium aluminum hydride yielded the diamine **12e**, providing in turn the dibenzoyl derivative **12f**. Addition of dimethyl acetylenedicarboxylate to **12b** yielded the bis(triazolyl) derivative **12g**. Base hydrolysis of **12c** gave the diol **12h**.[18,19]



12a, X = OCH_3
b, X = N_3
c, X = $OCOCH_3$
d, X = CN
e, X = NH_2
f, X = $NHCOC_6H_5$



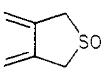
h, X = OH

The preparation and properties of compounds **12** have already been described in some detail.[2] Complementary information, including the preparation of Diels–Alder adducts, is given in the Experimental Section.

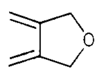
Monosubstituted derivatives of **1** were sometimes observed, or were prepared on purpose by the use of 1 equiv of the nucleophile. These reactions needed, however, a careful separation of the mono derivative from the bis derivative and from the starting material and were, usually, not pursued.

Five-Membered Heterocycles with Exocyclic Cis-Fixed Dienes. Conjugated dienes with a permanent cisoid geometry, such as 1,2-dimethylene cyclic or heterocyclic compounds, have been of interest in regard to their photoreactivity in producing strained polycyclic cyclobutenes,[20] to their cycloaddition reactions in competitive 1,2 and 1,4 additions,[21] and to their polymerization reactions in producing all-cis polymers.[22] The formation of such exocyclic dienes from **1** could proceed in two ways: either directly, by displacement of the two bromines by one heteroatom, or indirectly, through a [4 + 2] cycloaddition followed by zinc-induced 1,4 elimination of bromine. We have used both methods in the production of such systems.

The direct method has furnished the three five-membered heterocyclic systems **13–15**.[2,3] Thus, reaction of **1** with sodium sulfide in ethanol produced 3,4-dimethylenethiolane (**13a**) in ca. 85% yield, as estimated by UV. Oxidation of **13a** with 1 or 2 mol of *m*-chloroper-



13a, $n = 0$
b, $n = 1$
c, $n = 2$



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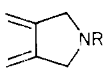

15a, R = CH_3
b, R = $CH(CH_3)_2$
c, R = $C(CH_3)_3$
d, R = C_6H_{11}
e, R = C_6H_5

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(13) Levek, T. J.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 1875–9, and leading references therein.

(14) Normant, H. *C. R. Hebd. Seances Acad. Sci.* **1954**, *239*, 1811–2.

(15) The attractive eventuality of thermally converting **8** into the linear isomer 1,9-decadien-5-yne, through a double Cope rearrangement, is not probable on the basis of calculated standard heats of formation, which favor the tetraene **8** by about 14.4 kcal/mol (Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968; pp 23–6, 178). We thank Professor M. J. Goldstein for a discussion of this matter.

(16) Gaoni, Y.; Leznoff, C. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 4940–5.

(17) Looker, B. E.; Sondheimer, F. *Tetrahedron* **1971**, *27*, 2567–71.

(18) Bailey, W. J.; Sorenson, W. R. *J. Am. Chem. Soc.* **1956**, *78*, 2287–90.

(19) Zahorsky, U. I.; Musso, H. *Justus Liebigs Ann. Chem.* **1973**, 1777–88.

(20) Aue, D. H.; Reynolds, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 2027–8.

(21) Bartlett, P. D.; Wingrove, A. S.; Owyang, R. *J. Am. Chem. Soc.* **1968**, *90*, 6067–70.

(22) Marvel, C. S.; Ryder, E. E. *J. Am. Chem. Soc.* **1955**, *77*, 66–8.

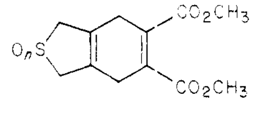
benzoic acid (CPBA) yielded the sulfoxide **13b** and the sulfone **13c**, respectively.

3,4-Dimethyleneoxolane (**14**)[23] was obtained from **1** in ca. 35% yield by reaction with alkaline bases in dimethyl sulfoxide.

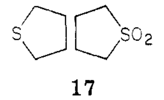
N-Alkyl- and *N*-aryl-3,4-dimethylenepyrrolidines (**15**) were prepared in 50–75% yields by reaction of **1** with primary amines in acetonitrile or methanol solution. Most of these pyrrolidine compounds were prepared concurrently with our work by an indirect method and were fully characterized.[24]

The heterocyclic dienes **13–15** are mostly unstable compounds, deteriorating rapidly in the free state. In cold solutions they are, however, stable for at least a 1-week period. Their purification was carried out by distillation or by chromatography on silica gel and eventual crystallization. They all undergo Diels–Alder additions with such dienophiles as dimethyl acetylenedicarboxylate, dimethyl azodicarboxylate, *N*-phenylmaleimide, and sulfur dioxide, to give adducts in high yields. All amines **15** gave also the corresponding methiodides by reaction with methyl iodide.[24] Two of the amines, **15a** and **15c**, could be photochemically cyclized to bicyclic systems.

Earlier attempts to prepare thiolane **13a** have failed, the corresponding thiophenes being produced in most cases.[22,25,26] We have obtained it now as a polymerizing liquid, which could be distilled in small batches and obtained pure for immediate use. It formed adduct **16a** with dimethyl acetylenedicarboxylate and adduct **17** with sulfur dioxide. Evidence for a 1,4 bromine addition to **13a** to form **18** was obtained by carrying out the reaction in the NMR tube: only two new singlets appeared, at δ 3.93 and 4.06, along with the disappearance of the original peaks (compare with 4.02 and 4.07 for the sulfone **3**[5]).



16a, $n = 0$
b, $n = 1$
c, $n = 2$



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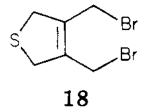
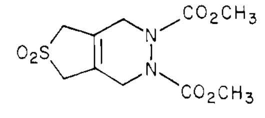


18

Oxidation of **13a** to the sulfoxide **13b** was carried out with CPBA in chloroform at 0 °C. Crystalline **13b** polymerized overnight, but its solutions were stable for several weeks. The ^{1}H NMR spectrum of **13b** exhibited one singlet for the ring protons, at δ 3.7, indicating a conformationally mobile system, with a low enantiomerization barrier.[27,28] At low temperatures, or through the addition of Eu(fod)$_3$, the singlet was resolved into an AB quartet. The free energy of activation, at an observed coalescence temperature of 15 ± 5 °C,[29] was calculated with the Eyring rate equation[28,30] to be 14.3 ± 0.3 kcal/mol, a value which agrees well with that of $\Delta G^{\ddagger}_{30} = 15.1$ kcal/mol for the more hindered 3,4-bis(1-methylethylidene)thiolane 1-oxide.[28]

Sulfone **13c** was obtained from **13a** by oxidation with 2 mol of CPBA. The solid sulfone was quite stable, being soluble after a few days at room temperature. Solutions of **13c** were stable, but traces of acid caused polymerization. Melting of the sulfone was observed only when a sample of it was introduced on to the hot plate at the right temperature; by warming below the melting point, high melting transformation products were formed. No evolution of sulfur dioxide, that could have transiently produced the 2,2′-bis(allyl) diradical, was observed to occur at any temperature. The same reluctance to expel sulfur dioxide was found in the 2,5-di-*tert*-butyl analogue of **13c**.[31]

Adducts **16b** and **16c** were obtained, respectively, from **13b** and **13c** and dimethyl acetylenedicarboxylate. Adduct **19** was obtained from **13c** and dimethyl azodicarboxylate.



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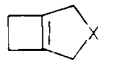

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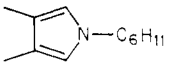
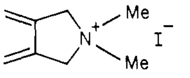


21

Irradiation of compounds **13–15** with a low-pressure mercury lamp was expected to produce strained heterobicyclic systems of type **20**. The oxa, thia, and aza analogues of **20** (X = O, S, NR), mainly with higher degrees of unsaturation and substitution, have been studied in recent years with regard to the special properties of the strained aromatic systems involved.[32,33] Compounds **20**, as derived from **13–15**, could be considered as potential precursors to such aromatic systems.

Irradiation of **13a** and **14** in pentane solutions produced, however, mainly insoluble, unidentified materials, with some of the starting material being recovered even after 5 days. Similar results were also obtained with the amines **15** in ether or pentane solutions, except for **15d**, where the isomeric pyrrole, **21**, could be isolated in 5% yield and identified through its mass and NMR spectra. This behavior of the amines **15** conforms with the known properties of aliphatic amines to undergo carbon–nitrogen bond cleavage under irradiation conditions with evolution of nitrogen and formation of amines and hydrocarbon mixtures, a behavior which seems to be ascribable to the free electrons on nitrogen.[34] A solution of the quaternized amine 1,1-dimethyl-3,4-dimethylenepyrrolidinium iodide (**22**) in methanol was therefore irradiated, producing 1,1-dimethyl-3-azoniabicyclo[3.2.0]hept-1(5)-ene iodide (**23**) in ca. 25% yield. The highly hygroscopic compound was characterized through its mass and NMR spectra. Irradiations of the amines **15** were then carried out in aqueous acidic solutions and the bicyclic products **24** could be isolated in 50–60% yields. These bicyclic amines are rather unstable, but they can be kept for long periods of time in aqueous acidic solutions or in dry organic solvents in the cold. They were characterized through their physical properties and through their picrates. In the GC appa-



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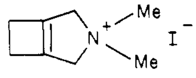

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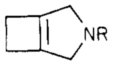

24a, R = CH$_3$
b, R = C(CH$_3$)$_3$

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(23) Bailey, W. J.; Miller, S. S. *J. Org. Chem.* **1963**, *28*, 802–5.

(24) (a) Ottenbrite, R. M.; Alston, P. V. *J. Heterocycl. Chem.* **1973**, *10*, 785–90. (b) Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1974**, *39*, 1115–8. See also: Gschwend, H. W.; Haider, H. H. *J. Org. Chem.* **1972**, *37*, 59–61.

(25) Marvel, C. S.; Nowak, R. M.; Economy, J. *J. Am. Chem. Soc.* **1956**, *78*, 6171–4.

(26) Fetter, E. *J. Diss. Abstr.* **1962**, *22*, 2985–6.

(27) Barbarella, G.; Garbesi, A.; Fava, A. *J. Am. Chem. Soc.* **1975**, *97*, 5883–9.

(28) Jelinski, L. W.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 281–2.

(29) It was difficult to be more precise on the coalescence temperature of the AB quartet.

(30) See Anderson, J. E.; Lehn, J. M. *Tetrahedron* **1968**, *24*, 137–49 for relations used to calculate k_c and $\Delta G^{\ddagger}$ at the coalescence temperature T_c.

(31) Beetz, T. Ph.D. Thesis, University of Groningen, 1975.

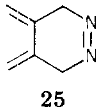
(32) See Bergman, R. G.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1973**, 214–5.

(33) (a) Garratt, P. J.; Neoh, S. B. *J. Org. Chem.* **1975**, *40*, 970–1, and references therein. (b) Garratt, P. J.; Neoh, S. B. *J. Am. Chem. Soc.* **1975**, *97*, 3255–7.

(34) (a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; pp 455-60. (b) Cundall, R. B.; Gilbert, A. "Photochemistry"; Appleton–Century–Crofts: New York, 1970; pp 119–20.

ratus, at a temperature of 200 °C, they underwent a thermal electrocyclic ring opening back to the starting materials **15**, as expected. The methiodide prepared from **24a** was identical with **23**, obtained directly from **22**.

Six-Membered Carbo- and Heterocycles. Reactions of dibromide **1** as a 1,3-diene in Diels–Alder cycloadditions lead to six-membered rings, which can then be further modified. One such sequence was connected with our intention to obtain an immediate precursor, **25**, of the 2,2′-bis(allyl) diradical (**26**). During the course of our work two other groups have, however, obtained stable derivatives of **25** and studied the formation and evolution of the corresponding diradicals.[13,35] Our approach to the synthesis of **25**, proceeding through hexahydropyridazine systems and presently described, was therefore not pursued to its end.



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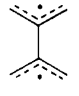
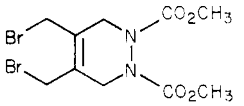


26

Reaction of **1** with dimethyl azodicarboxylate provides pyridazine **27**, in 60–70% yield. Debromination of **27** with zinc–copper couple produces **28**, in similar yields, and **29** is then obtained from **28** by base hydrolysis. Diene **28** is an unstable compound which polymerizes readily, even in solution, but from which Diels–Alder adducts, such as **30**, could be obtained. Hydrazine **29** was likewise very unstable. Stabilization of the system was achieved through diene–iron tricarbonyl type complexes. Complex **31**, prepared by reaction of **28** with diiron nonacarbonyl, only slowly decomposes in solution and is stable in the solid state.[36] An unprolonged hydrolysis of **31** with potassium hydroxide in methanol yielded the monoester **32**, while a longer reaction time led to **33**. Complex **33** was stable in dry ether solution under argon. No definite products could be obtained from it in some oxidation experiments in anhydrous conditions, but in the presence of humidity,[37] complex **34** could be isolated after air oxidation in an overall yield of ca. 45% from **31** and characterized through its mass and ^{1}H NMR spectra.



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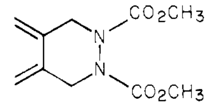

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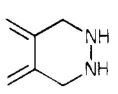

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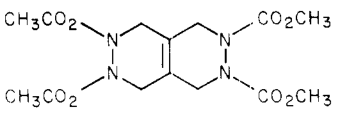

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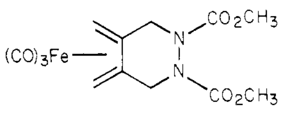

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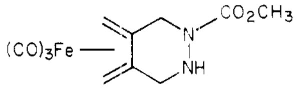

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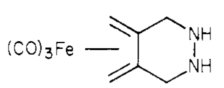

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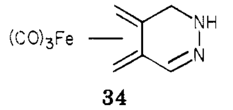
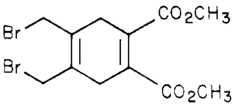


34

The application of **1** to the construction of carbocyclic systems is illustrated by the following sequence. The Diels–Alder adduct of **1** with dimethyl acetylenedicarboxylate, **35**, was debrominated with zinc–copper couple to the exocyclic diene **36**. A second addition of dimethyl acetylenedicarboxylate to the latter provided then the tetrahydronaphthalene derivative **37** in an overall 73% yield from **35**.



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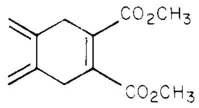

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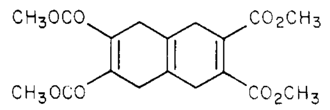
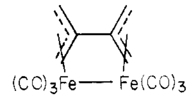


37

Reaction of 1 with the Iron Carbonyls. Considering **1** as a precursor of the 2,2′-bis(allyl) diradical (**26**) and appreciating that such unstable species may be stabilized by π complexation with transition metals,[38] we undertook a study of the reaction of **1** and **2** with the iron carbonyls. Upon reaction with diiron nonacarbonyl in hexane, both bromides were found, indeed, to produce the known complex **38** of diradical **26**, in ca. 10 and 20% yield, respectively. In the case of dibromide **1**, complex **38** was accompanied, however, by two dimeric trimethylenemethane-type complexes,[39] **39** and **40**, formed in 7.5 and 2% yield, respectively.



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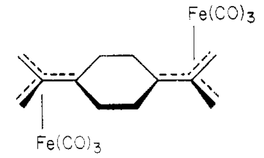

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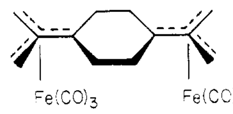

40

Complex **38** has been obtained previously by reaction of allene with iron carbonyls,[40,41] and similar complexes were derived from phenylallene.[42] Allene and oligo(allenes) have furthermore been the source of a large number of transition-metal complexes with a considerable variety of bonding schemes such as the binuclear mixed type iron complexes of an allene trimer.[43]

Complexes **39** and **40** derive from a bis(allyl) diradical dimer, formally an allene tetramer. Their structures were determined by physical and chemical methods. Both showed very similar mass spectral fragmentation patterns, with a molecular ion peak at *m/e* 440 and ions corresponding to the loss of up to six carbonyl units. The ^{1}H NMR of both isomers showed three singlet signals at lower field than diene-type complexes, with very similar chemical

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(35) Beetz, T.; Kellogg, R. M. *J. Am. Chem. Soc.* **1973**, 95, 7925–6.

(36) The dynamic phenomena associated with rotation about the N–CO bond, with nitrogen inversion and with ring reversal in hexahydropyridazine systems,[37] were observed also in **28** and **31** through their temperature-dependent ^{1}H NMR spectra and will be further studied.

(37) See Bittner, E. W.; Gerig, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 913–22.

(38) Kritskaya, I. I. *Russ. Chem. Rev.* **1972**, 41, 1027–45.

(39) Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464–70.

(40) Nakamura, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 543–7.

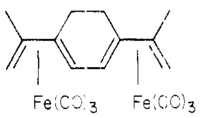
(41) Ben-Shoshan, R.; Pettit, R. *Chem. Commun.* **1968**, 247–8.

(42) Otsuka, S.; Nakamura, A.; Tani, K. *J. Chem. Soc. A* **1968**, 2248–53.

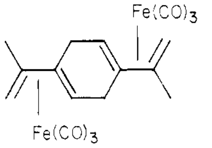
(43) Otsuka, S.; Nakamura, A.; Tani, K. *J. Chem. Soc. A* **1971**, 154–9, and references cited therein.

shifts and in a ratio of 1:2:1. The UV spectra of the two isomers were very similar, and so were the IR spectra which showed resolved absorption bands in the carbonyl region at slightly higher frequencies than the isomeric diene complexes later derived. The possibility of **39** and **40** being complexes of the tetraene **6** was eliminated on the basis of the ^{13}C NMR spectra, which showed four types of skeletal carbons and not three, as would be expected for a bis(diene)-type complex of **6**. The configuration of the iron nuclei was determined through X-ray measurement of the cell units of the more abundant isomer. This showed a centrosymmetric molecular structure: space group $P2_1/a$, unit cell parameters: a = 12.99 Å, b = 11.35 Å, c = 7.14 Å, $\beta \simeq 100°$, ρ = 1.41 g/cm^3, Z = 2.[44] This isomer was therefore assigned the transoid centrosymmetric structure **39**, while the cisoid structure **40** was assigned to the spectroscopically very similar, minor isomer.

Protonation and deprotonation of **39** and **40** by treatment with concentrated sulfuric acid followed by dilution with water[39] yielded, from each, a 1:1 mixture of the bis(diene) complexes **41** and **42**. Complete conservation of the relative configuration of the iron nuclei was observed during this isomerization. This was concluded from the absence of any scrambling during the process, while the probability of total inversion in the isomerization of both **39** and **40** was rejected. The transoid **41a** and **42a** were thus cleanly obtained from **39** and the cisoid **41b** and **42b** from **40**. The ^1H NMR spectra of the four isomers allowed a clear distinction between the conjugated complexes **41**, where the ring vinylic protons appeared as sharp singlets, and the unconjugated **42**, where they appeared as a double doublet (X part of an ABX system formed with the ring methylenes).



41a, *trans*-diiron
b, *cis*-diiron



42a, *trans*-diiron
b, *cis*-diiron

Oxidation of **42a** with ceric ammonium nitrate in methanol[45] yielded a mixture of two hydrocarbons in a ratio of ca. 1:8 and in a total yield of 95%. These were separated by preparative GC and identified as 1,4-diisopropenylbenzene (major component; identical with an authentic sample[46]) and 1,4-diisopropenyl-1,4-cyclohexadiene,[47] identified through its ^1H NMR spectrum and through a high-resolution mass spectrum.

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and were uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord 137 or 457A grating spectrometer and ultraviolet spectra with a Cary 14 spectrophotometer. Proton NMR spectra were measured in deuteriochloroform with a Varian A-60 spectrometer or a Bruker 90 spectrometer and are given in δ units downfield from Me_4Si as internal standard. The Bruker instrument was also used for recording ^{13}C NMR spectra. Mass spectra were determined with Atlas MAT 731 or MAT CH4 spectrometers. TLC was done on Merck Kieselgel 60-F254 precoated aluminum plates. The silica gel for column chromatography was Merck Kieselgel 60, 70–230 mesh. Analytical and preparative gas chromatographies (GC) were done with an Aerograph A-90-P instrument, usually with 10% DC 710 on Chromosorb W, with 5 or 10 ft columns, 0.25 to 0.75 in. diameter. Photolysis was done with a low-pressure mercury lamp, Hanau Tnn 15/32, using a Vycor filter. Elemental analyses were performed by Mr. R. Heller of The Weizmann Institute of Science, Microanalytical Laboratory.

Diels–Alder adducts of conjugated dienes were prepared by reacting them with an equivalent amount of the dienophile, in the indicated solvent and at reflux temperature. The yields were, usually, 70–90%.

Standard workup of reactions means adding water or ice, extracting several times with ether, washing the combined ether extracts with water, eventually with dilute acid or base, and with a saturated sodium chloride solution, drying on an anhydrous salt, and carefully evaporating the solvent at reduced pressure with a rotating evaporator.

2,3-Bis(bromomethyl)-1,3-butadiene (1). Tetrabromide **2**[6] (10 g, recrystallized from ethyl acetate) was refluxed in ether (100 mL) for 20 min, with good stirring, in the presence of zinc–copper couple[48] (5 g). HMPT (10 mL) and additional zinc–copper couple (2 g) were then added to the stirred, refluxing mixture. Further portions of the metal, 2 g each, were added after every additional hour, the total reflux time being 3.5 to 4.5 h. Workup was carried out by filtering the reaction mixture on Celite filter-aid and evaporating most of the ether from the clear, colorless solution under reduced pressure with mild warming. The residue was dissolved in pentane (100 mL) and washed once with a saturated ammonium chloride solution, three times with water, and once with a saturated sodium chloride solution. After the solution was dried (sodium sulfate), the solvent was evaporated to dryness and the solid residue was again dissolved in pentane (50 mL) with slight warming and filtered from any floating polymeric material. Evaporation of the pentane yielded 5.1–5.3 g of colorless, crystalline **1** (85–88%). Crystallization from pentane yielded 4.2–4.4 g (70–73%) of pure **1**:[5] mp 57–58 °C; δ 4.20 (s, 4 H), 5.53 (s, 2 H), 5.58 (s, 2 H); ν_{max} (CCl_4) 1600, 920 cm^{-1}; λ_{max} (isooctane; ethanol) 225 nm (ϵ 10 000).

This procedure can be scaled up to at least 50 g of **2**, with similar results.

2,3-Bis(tosylmethyl)-1,3-butadiene (5a, *n* = 1), 2-(Bromomethyl)-3-(tosylmethyl)-1,3-butadiene (5f, *n* = 1), and 3,6-Dimethylene-2,7-bis(tosylmethyl)-1,7-octadiene (5a, *n* = 2). The combined mother liquors from crystallization of a few batches of **1** were evaporated to dryness and the oily residue (2.3 g) was warmed at 60 °C in HMPT (15 mL) with sodium *p*-toluenesulfinate (2.4 g) for 4 h. Water was slowly added to the still warm mixture and a precipitated solid was filtered and recrystallized from ethanol to yield **5a** (n = 1): mp 178–179 °C; δ 2.44 (s, 6 H), 4.05 (s, 4 H), 5.00 (s, 2 H), 5.46 (s, 2 H), 7.33 and 7.77 (AB-like pattern, 4 H); m/e 235 ($M^+ - C_7H_7SO_2$, base), 181, 169, 139, 131, 119, 91.

Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68. Found: C, 61.67; H, 5.51.

The combined filtrate and washings of **5a** (n = 1) yielded, after a standard workup, a residue that was chromatographed on silica gel (50:1). Only two solid products were obtained upon elution with dichloromethane. The first was the monosulfone **5f** (n = 1): mp 123–124 °C (ethanol); δ 2.43 (s, 3 H), 4.05 (s, 2 H), 4.13 (s, 2 H), 5.15, 5.36, 5.41 and 5.58 (four singlets for the four different vinylic protons), 7.33 and 7.78 (AB-like pattern, 4 H).

Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80. Found: C, 49.45; H, 4.69.

The second solid eluted from the column was the disulfone **5a** (n = 2) deriving from **4**: mp 137–138 °C; δ 2.26 (s, 4 H), 2.41 (s, 6 H), 4.03 (s, 4 H), 5.03 (m, 6 H), and 5.36 (s, 2 H; vinylic protons), 7.33 and 7.76 (AB-like pattern, 8 H); m/e 315 ($M^+ - C_7H_7SO_2$), 235 (base, $M^+/2$).

Anal. Calcd for $C_{26}H_{30}O_4S_2$: C, 66.35; H, 6.42. Found: C, 66.05; H, 6.45.

Debromination of 1 in DMF. To a measured aliquot from a 0.8 M solution of **1** in dry DMF was added a calculated equal weight of zinc–copper couple. With good stirring, the temperature

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[44] Preliminary X-ray measurements were performed in the Department of Structural Chemistry of this Institute by Mr. J. Halfon.

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rose in 0.5 h to 48–50 °C and then slowly dropped. Stirring was continued at room temperature for 20 h. The mixture was filtered on Celite and the precipitate was washed with ether. Amonium chloride solution was added to the combined filtrate, and washing and standard workup procedure then yielded a mixture of about 20 components (TLC in pentane and pentane–ether 1:1) in a total 90% yield.

Partial separation was achieved by chromatography on silica gel, in a ratio of 200:1, with pentane as eluent.

The first eluted fraction consisted of a mixture of two compounds, which appeared as one spot on TLC. They were separated by GC on a column of 25% β,β-oxidopropionitrile on Chromosorb P, 10 ft × 0.25 in.; 2,7-dimethyl-3,6-dimethylene-1,7-octadiene (**5b**, $n = 2$) was obtained as a polymerizing liquid (12–15% yield), δ 1.93 (6 H), 2.46 (4 H), 5.00 (2 H), 5.10 (2 H; all singlets); ν_{max} ($CHCl_3$) 3060, 2920, 1600, 890 cm^{-1}; *m/e* 162 (M^+), 79 (base).

A bis adduct of **5b** ($n = 2$) with *N*-phenylmaleimide, 1,2-bis-[4-methyl-1,2-(*N*-phenyldicarboximido)-4-cyclohexen-5-yl]ethane (**7**, $n = 2$), was prepared in benzene and was recrystallized from ether, crystallizing apparently with one molecule of water: mp 161–163 °C; δ 1.73 (s, 6 H), 2.03 (s, 4 H), 2.25–2.83 (m, 8 H, allylic ring protons), 3.07 (m, 4 H, angular protons), 7.27 (m, 10 H); ν_{max} (KBr) 1700, 1360, 1190, 790, 720 cm^{-1}; *m/e* 508 (M^+), 255 ($M^+/2$ + 1), 254 ($M^+/2$), 107 (base), 91.

Anal. Calcd for $C_{32}H_{32}N_2O_4{\cdot}H_2O$: C, 73.00; H, 6.46; N, 5.32. Found: C, 73.11; H, 6.35; N, 5.41.

1,2,5,6-Tetramethylenecyclooctane (**6**)[11] was the second substance obtained from the GC separation (2–5% yield): δ 2.4 (s, 8 H), 4.83 (d, J = 2 Hz, 4 H), 4.93 (d, J = 2 Hz, 4 H); *m/e* 160 (M^+), 132 (base).

A bis adduct with *N*-phenylmaleimide was prepared in benzene: tricyclo[10.4.0.0^{4,9}]hexadeca-1(12),4(9)-diene-6,7:14,15-bis(*N*-phenyldicarboximide), mp 186–187 °C (ethyl acetate); δ 2.00–2.62 (m, 16 H, allylic ring protons), 3.07 (m, 4 H, angular protons), 7.27 (m, 10 H); *m/e* 506 (M^+, base), 253 ($M^+/2$), 106, 91.

2,11-Dimethyl-3,6,7,10-tetramethylene-1,11-dodecadiene (**5b**, $n = 3$) was eluted second from the silica gel column and obtained in 6–10% yield: δ 1.91 (6 H), 2.41 (8 H), 4.95 (6 H), 5.15 (6 H; all singlets); ν_{max} ($CHCl_3$) 1605, 910 cm^{-1}; *m/e* 242 (M^+), 91, 79.

A tris adduct with *N*-phenylmaleimide was prepared in benzene, 4,5-bis{2-[4-methyl-1,2-(*N*-phenyldicarboximido)-4-cyclohexen-5-yl]ethyl}-4-cyclohexene-1,2-(*N*-phenyldicarboximide) (**7**, $n = 3$): mp ca. 100 °C (ether); δ 1.70 (s, 6 H), 2.00 (s, 8 H), 2.20–2.78 (m, 12 H), 3.38 (m, 6 H), 7.40 (m, 15 H); *m/e* 761 (M^+), 508, 507, 255, 254, 107 (base), 91.

Anal. Calcd for $C_{48}H_{47}N_3O_6{\cdot}H_2O$: C, 73.92; H, 6.33. Found: C, 73.80; H, 6.24.

2,15-Dimethyl-3,6,7,10,11,14-hexamethylene-1,16-hexadecadiene (**5b**, $n = 4$) was eluted next and obtained in 6–10% yield as a polymerizing oil: δ 1.9 (6 H), 2.40 (12 H), 4.91 (8 H), 5.18 (8 H; all singlets); *m/e* 322 (M^+), 247, 159, 131, 105, 91 (base).

When the debromination reaction of **1** was carried out under the above conditions but for a total period of 2 h, a different mixture was obtained. Separation on silica gel as above furnished undetermined amounts of **5b** oligomers, **6**, unchanged **1**, and also the following isolated products.

2-Bromomethyl-7-methyl-3,6-dimethylene-1,7-octadiene (**5c**, $n = 2$) was obtained as a lachrymatory, polymerizing liquid in 3–5% yield; δ 1.93 (s, 3 H), 2.45 (s, 4 H), 4.20 (s, 2 H, bromomethyl protons), 4.90 (s, 2 H), 5.03 (s, 2 H), 5.26 (m, 4 H). A monosulfone was prepared by warming **5c** ($n = 2$) with excess sodium *p*-toluenesulfinate in HMPT at 60 °C for 2 h. Addition of water, extraction with ether, and purification by elution from a short column of silica gel with ether–pentane 7:3, followed by crystallization from ether, yielded 7-methyl-3,6-dimethylene-2-(tosylmethyl)-1,7-octadiene (**5e**, $n = 2$) in 70–80% yield: mp 75–76 °C; δ 1.91 (s, 3 H), 2.35 (s, 3 H, aromatic methyl), 2.45 (s, 4 H), 4.06 (s, 2 H, $-CH_2SO_2-$), 5.04 (m, 7 H), 5.43 (s, 1 H), 7.33 and 7.80 (AB-like pattern, 4 H); ν_{max} (KBr) 1600, 1285, 1275, 1140, 875 cm^{-1}; *m/e* 161 ($M^+ - CH_3C_6H_4SO_2$), 160, 145, 119, 105, 91 (base).

Anal. Calcd for $C_{19}H_{24}O_2S$: C, 72.11; H, 7.64. Found: C, 71.95; H, 7.55.

2-(Bromomethyl)-11-methyl-3,6,7,10-tetramethylene-1,11-dodecadiene (**5c**, $n = 3$) was obtained next from the silica gel column as a lachrymatory polymerizing liquid in 3–5% yield; δ 1.93 (s, 3 H), 2.43 (s, 8 H), 4.18 (s, 2 H), 5.00 (s, 4 H), 5.15 (s, 4 H), 5.36 (m, 4 H). A monosulfone was obtained as above: 11-methyl-3,6,7,10-tetramethylene-2-(tosylmethyl)-1,11-dodecadiene (**5e**, $n = 3$), mp 35–36 °C (hexane–ether); δ 1.95 (s, 3 H), 2.35 (s, 3 H), 4.10 (s, 2 H), 5.05 (m, 11 H), 5.46 (s, 1 H), 7.33 and 7.80 (AB-like pattern, 4 H); ν_{max} ($CHCl_3$) 1600, 1320, 1310, 1150, 900 cm^{-1}; *m/e* 241 ($M^+ - CH_3C_6H_4SO_2$), 167, 156, 139, 91, 55 (base).

Anal. Calcd for $C_{25}H_{32}O_2S$: C, 75.71; H, 8.13. Found: C, 75.42; H, 8.29.

2,11-Bis(bromomethyl)-3,6,7,10-tetramethylene-1,11-dodecadiene (**5d**, $n = 3$) was also obtained as a lachrymatory, polymerizing liquid, in 4–7% yield: δ 2.43 (s, 8 H), 4.16 (s, 4 H), 4.93–5.50 (m, 12 H). A disulfone was obtained as above: 3,6,7,10-tetramethylene-2,11-bis(tosylmethyl)-1,11-dodecadiene (**5a**, $n = 3$), mp 90–91 °C (hexane–ether); δ 2.31 (s, 8 H), 2.43 (s, 6 H), 4.06 (s, 4 H), 5.03 (m, 10 H), 5.41 (s, 2 H), 7.33, 7.80 (AB-like pattern, 8 H); ν_{max} (KBr) 1590, 1320, 1310, 1160, 900 cm^{-1}; *m/e* 395 ($M^+ - CH_3C_6H_4SO_2$), 305, 234, 156 (base).

Anal. Calcd for $C_{32}H_{38}O_4S_2$: C, 69.78; H, 6.95. Found: C, 69.55; H, 6.85.

Debromination of **1** was also carried out by stirring for 20 h with zinc–copper couple in ether–D_2O 4:1, instead of DMF. Oligomers **5** (X = Y = D) were obtained, of which the lowest member, $n = 2$, was isolated as described. Its ^1H NMR spectrum, similar to that of **5b** ($n = 2$), showed an approximate 1:1 ratio of the vinylic methyls at δ 1.93 to the aliphatic methylenes at δ 2.46; ν_{max} (CCl_4) 3060, 3000, 2140 (C–D stretching), 1440, 900 cm^{-1}.

A bis adduct with *N*-phenylmaleimide, mp 162–163 °C (ether), was analyzed by mass spectrometry: *m/e* 510 (M^+), 256, 255, 108 (base), 91.

4,5-Dimethylene-1,7-octadiene (8) and 4,5,8,9-Tetramethylene-1,11-dodecadiene (9). A solution of vinylmagnesium chloride in THF (30 mL), prepared from magnesium (1.25 g, 0.05 mol) and vinyl chloride (3.5 g, 0.056 mol), was transferred under nitrogen into a dropping funnel and added dropwise, at room temperature, into a solution of **1** (4.8 g, 0.02 mol) in THF (30 mL) containing cuprous chloride (50 mg). A spontaneous warming was controlled by a slight external cooling with tap water. After stirring for another 2 h at room temperature, the clear solution was worked up by adding half-saturated ammonium chloride solution, extracting with ether, washing with water and with a saturated sodium chloride solution, and drying (sodium sulfate). Careful evaporation of the solvent yielded a mixture of two compounds (2.2 g) in a ratio of ca. 8:3 (GC), which could be easily separated by distillation over a short path.

The first fraction, bp 100–110 °C (bath) (20 torr), consisted of the tetraene **8** (1.07 g, 40% yield); δ 3.02 (d, J = 6.5 Hz, 4 H), 4.85–5.25 (m, 8 H), 5.55–6.20 (m, 2 H); ν_{max} ($CHCl_3$) 1639, 1600, 1000, 910 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.33; H, 10.72.

An adduct of **8** with *N*-phenylmaleimide was prepared in benzene: 4,5-bis(2-propenyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide): mp 46–47 °C (hexane); *m/e* 307 (M^+), 292, 278, 173, 159, 145.

Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.33; H, 6.80; N, 4.43.

The following fraction from the distillation of the crude reaction mixture, boiling up to 110 °C (bath) (1 torr), was neglected.

The third fraction, bp 110–120 °C (bath) (1 torr), consisted of the hexaene **9** (0.22 g, 10% yield); δ 2.85 (s, 4 H), 3.00 (d, J = 6.5 Hz, 4 H), 4.85–5.25 (m, 12 H), 5.50–6.20 (m, 2 H); ν_{max} ($CHCl_3$) 1645, 1600, 900 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}$: C, 89,65; H, 10.35. Found: C, 89.42; H, 10.55.

An adduct of **9** with *N*-phenylmaleimide was prepared in benzene and obtained as an amorphous resin after purification on silica gel with dichloromethane (mixture of diastereomers). Crystals of apparently one pure diastereomer formed, however, by slow evaporation of a chloroform–ether solution: 1,2-bis[4-(2-propenyl)-1,2-(*N*-phenyldicarboximido)-4-cyclohexen-5-yl]-ethane: mp 148–150 °C; *m/e* 560 (M^+), 280.

Anal. Calcd for $C_{36}H_{36}N_2O_4$: C, 77.12; H, 6.47. Found: C, 77.02; H, 6.40.

4,5-Dimethylene-1,7-octadiyne (10) and 4,5,10,11-Tetramethylene-1,7,13-tetradecatriyne (11). A solution of ethynylmagnesium bromide in THF (25 mL) was prepared from magnesium (1 g, 0.042 mol), ethyl bromide (5 g, 0.046 mol), and acetylene. Cuprous chloride (50 mg) was added, and a solution of **1** (4 g, 0.017 mol) in THF (20 mL) was then dropped in during 15 min with stirring. More cuprous chloride (25 mg) was added and the stirred mixture was heated in a water bath at 55–60 °C for 2 h. Workup[16] then yielded 1.9 g of a crude mixture, which was separated by chromatography on silica gel (150 g; elution with hexane–ether 9:1; monitoring by GC).

The first substance eluted was the liquid diyne **10** (1.01 g, 46%, pure by GC), freezing below 0 °C. A small sample was rapidly distilled at 50 °C (bath temperature) (1 torr); δ 2.16 (m, 1 H), 3.20 (m, 4 H), 5.30 (s, 2 H), and 5.50 (s, 2 H); ν_{max} (CHCl$_3$) 3310, 2120 (weak), 1600, 910 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.82; H, 7.64.

An adduct with *N*-phenylmaleimide was prepared in benzene: 4,5-bis(2-propynyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide), mp 103–104 °C (ethanol).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65. Found: C, 78.93; H, 5.60.

The second substance eluted from the column was the unstable solid **11**: mp 58–60 °C (pentane; 185 mg, 9.5%); δ 2.15 (m, 2 H), 3.20 (s, 8 H), 5.26 (s, 4 H), and 5.46 (s, 4 H); ν_{max} (KBr) 3280, 1595, 890 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.70.

2,3-Bis(methoxymethyl)-1,3-butadiene (12a). (a) A solution of **1** (2.5 g) in methanol (30 mL) was added dropwise at room temperature into a solution of sodium methoxide (prepared from 0.5 g of sodium and 10 mL of methanol) and the whole was refluxed for 20 min. TLC showed then the absence of **1**. Evaporation of most of the methanol at reduced pressure followed by standard workup yielded 955 mg of practically pure **12a**, according to GC and NMR. Distillation, bp 50–55 °C (bath) (1 torr), gave 820 mg (56%) of pure **12a**: δ 3.35 (6 H), 4.14 (4 H), 5.29 (2 H), 5.36 (2 H; all singlets); ν_{max} (CHCl$_3$) 1604, 1100, 910 cm^{-1}; λ_{max} (isooctane) 224 nm (ε 14 900).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.91. Found: C, 67.33; H, 9.81.

An adduct with *N*-phenylmaleimide was prepared by warming crude **12a** (355 mg) with the imide (430 mg) in benzene (5 mL) for 15 min. The resulting solution was eluted from silica gel (10 g) with benzene–ether 1:1. The product obtained (492 mg) was recrystallized from ethanol, yielding 4,5-bis(methoxymethyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide), mp 61–62 °C.

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71. Found: C, 68.43; H, 6.60.

An adduct with maleic anhydride was likewise prepared from crude **12a** and the crude adduct was directly recrystallized from hexane to yield 3,4-bis(methoxymethyl)-4-cyclohexene-1,2-dicarboxylic anhydride, mp 93–94 °C.

Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.55; H, 6.54.

(b) A lower yield of distilled **12a** was obtained from the reaction of **1** (2.3 g, in 30 mL of methanol) with sodium hydroxide (1 g, in 5 mL of water; 15 min reflux and workup as above).

2,3-Bis(azidomethyl)-1,3-butadiene (12b). To a solution of **1** (2.3 g) in ethanol (25 mL) was added sodium azide (1.3 g) dissolved in water (3 mL) and the total was lightly refluxed for 15 min. TLC and GC indicated the end of the reaction. Standard workup yielded 1.4 g (89%) of **12b** as a liquid product, quite pure by GC and NMR. A small sample was distilled from bulb to bulb, bp 75–80 °C (bath) (1 torr); δ 4.00 (4 H), 5.40 (2 H), 5.46 (2 H; all singlets); ν_{max} (CHCl$_3$) 2100, 1215, 910 cm^{-1}; λ_{max} (isooctane) 220, 282 nm (ε 14 100, 49). A sample of a few milligrams exploded upon warming in the microanalysis apparatus and shattered a quartz tube. Otherwise, **12b** was rather stable toward polymerization in solution, or in the free state below 5 °C.

Upon addition of dimethyl acetylenedicarboxylate in excess (over 2 equiv) to a solution of **12b** in chloroform, followed by 30-min reflux, evaporation of the solvent and recrystallization from ethanol, a bis(triazole) was obtained: 2,3-bis[(4,5-bis(methoxycarbonyl)-1*H*-1,2,3-triazol-1-yl)methyl]-1,3-butadiene (**12g**): mp 137–138 °C; δ 3.94 and 3.98 (6 H, OCH$_3$), 5.00 (s, 2 H), 5.47 (s, 6 H, 2 methene protons and 4 methylene protons, resolved into two singlets by addition of Eu(fod)$_3$); ν_{max} (KBr) 1724, 1280, 1248, 1230, 1060, 920 cm^{-1}; λ_{max} (ethanol) 217 nm (ε 24 300); *m/e* 448 (M$^+$), 417, 389, 264 (base; M$^+$ − one triazole unit), 250.

Anal. Calcd for $C_{18}H_{20}N_6O_8$: C, 48.21; H, 4.50; N, 18.74. Found: C, 48.11; H, 4.41; N, 19.00.

2,3-Bis(aminomethyl)-1,3-butadiene (12e). To a crude, dried ether solution of **12b**, prepared as described above, was added powdered lithium aluminum hydride in excess. A strong gas evolution started after a few minutes. The reaction mixture was stirred at room temperature for 30 min and then worked up by slow addition of saturated sodium sulfate solution, until a well-separated precipitate formed. Upon suction filtration, a solid form of **12e** precipitated from the cooling ether solution. It was filtered and dried over phosphorus pentoxide under normal pressure, mp 31–32 °C. Upon applying vacuum or by a longer stay over phosphorus pentoxide the product liquefied. Upon dissolution of the solid in chloroform, water was observed to separate. Upon distillation, bp 75–80 °C (bath temperature) (25 torr), anhydrous **12e** was obtained: δ 1.60 (4 H, amino protons), 3.50 (4 H), 5.20 (4 H; all singlets); ν_{max} (CHCl$_3$) 3330, 2930, 1620, 905 cm; λ_{max} (ethanol) 224 nm (ε 12 900).

The molecular extinction coefficient of the solid, when calculated for a monohydrate, was the same as that of distilled **12e**.

A bisamide was obtained by addition of benzoyl chloride to a solution of **12e** in 1 N sodium hydroxide: 2,3-bis(benzamidomethyl)-1,3-butadiene (**12f**): mp 201–202 °C (ethanol–benzene); ν_{max} (KBr) 3300, 1630, 910 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29. Found: C, 75.13; H, 6.36.

2,3-Bis(acetoxymethyl)-1,3-butadiene (12c).[18] To a solution of crude **1** (23 g, 0.096 mol) in acetic acid was added anhydrous sodium acetate (40 g, 0.75 mol) and the mixture was refluxed for 2 h. After the mixture was cooled, water (1 L) was added and extraction was carried out with ether (4 × 100 mL). Standard workup yielded 18 g of crude material, which was chromatographed on silica gel (300 g). Elution with ether–hexane 1:9 gave an undetermined amount of foreign substances. Continued elution, with ether–hexane 1:4, furnished 10.5 g (55%) of **12c** as a semisolid mass. Recrystallization from pentane yielded 8.4 g (44%) of pure **12c**, mp 42–43 °C (lit.[18] 43–44 °C).

Two of the components of the total reaction mixture, which preceded **12c** from the column, were identified through their ^{1}H NMR spectra as the monosubstituted 2-acetoxymethyl-3-(bromomethyl)-1,3-butadiene, δ 2.08 (3 H), 4.18 (2 H), 4.82 (2 H), 5.36 (1 H), 5.48 (2 H), 5.54 (1 H; all singlets), and 2,7-bis(acetoxymethyl)-3,6-dimethylene-1,7-octadiene, deriving from **4**, δ 2.06 (6 H), 2.43 (4 H), 4.77 (4 H), 5.05 (2 H), 5.12 (2 H), 5.28 (4 H; all singlets). These two compounds were not further characterized.

2,3-Bis(hydroxymethyl)-1,3-butadiene (12h).[18] To a solution of **12c** (9.6 g) in ethanol (30 mL) was added 40 mL of 3 N sodium hydroxide solution. The exothermic reaction which ensued was allowed to subside to room temperature and was worked up after 2 h by evaporation of most of the ethanol, saturation with potassium carbonate, and extraction with ether–dichloromethane 3:1. Evaporation of the solvent yielded quite pure **12h** (5.3 g, 95%) which was recrystallized from dichloromethane, mp 64–65 °C.[18]

2,3-Bis(cyanomethyl)-1,3-butadiene (12d).[49] Dibromide **1** (1.2 g) and potassium cyanide (1 g) were slightly warmed in HMPT–water. Standard workup furnished an estimated, though undetermined, high yield of **12d**, which was recrystallized from hexane–ether, mp 74–75 °C.

3,4-Dimethylenethiolane (13a). To a solution of **1** (4.5 g) in absolute ethanol (50 mL) was added 2 g of recrystallized anhydrous sodium sulfide and the mixture was stirred at room temperature for 2 h. Standard workup yielded an ethereal solution of **13a**, formed in 80–85% yield, as estimated by UV on the basis of ε 6000 at 240 nm for the pure compound. Pure **13a** was obtained by evaporation of the solvent and distillation: bp 31–33 °C (1.5 torr); δ 3.61 (4 H), 5.01 (2 H), 5.45 (2 H; all singlets); ν_{max} (CHCl$_3$) 910 cm^{-1}; λ_{max} (ethanol) 240 nm (ε 6000). Thiolane **13a** polymerized rapidly in the free state and was therefore kept in cold solutions.

An adduct with dimethyl acetylenedicarboxylate was prepared in methanol and recrystallized from hexane: dimethyl 3-thia-

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(49) Stetter, H.; Tresper, E. *Justus Liebigs Ann. Chem.* 1971, *746*, 1–5.

bicyclo[4.3.0]nona-1(5),7-diene-7,8-dicarboxylate (**16a**), mp 136–137 °C; δ 3.08 (4 H), 3.73 (4 H), 3.83 (6 H; all singlets); $\nu_{\max}$ (KBr) 1730, 1270, 1060 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.69; H, 5.55; S, 12.59. Found: C, 56.88; H, 5.40; S, 12.77.

An adduct of **13a** with sulfur dioxide was prepared by introducing a large excess of the gas (3 g) into a pressure bottle containing **13a** (0.4 g), ether (20 mL), and hydroquinone (0.05 g). The bottle was stoppered and allowed to stand overnight at room temperature. A white substance that precipitated was filtered and recrystallized twice from ethanol, yielding 3,7-dithiabicyclo[3.3.0]oct-1(5)-ene 3,3-dioxide (**17**; 0.3 g, 47%); mp 194 °C (sealed capillary); δ 3.80 (s, all protons); δ (C_5D_5N) 3.67 (s, 4 H) and 3.93 (s, 4 H); $\nu_{\max}$ (KBr) 1315, 1160, 1140 cm^{-1}; *m/e* 176 (M$^+$, base), 112, 111.

Anal. Calcd for $C_6H_8O_2S_2$: C, 40.91; H, 4.58; S, 36.34. Found: C, 40.98; H, 4.42; S, 36.50.

3,4-Dimethylenethiolane 1-Oxide (13b). Into an ice-cooled, stirred solution of **13a** (4.6 g) in dry chloroform (100 mL) was added dropwise a solution of 85% CPBA (8.5 g) in chloroform (25 mL). After stirring for 30 min at 0 °C, the solution was washed with sodium sulfite solution and with 5% sodium carbonate solution and dried (calcium chloride). The crude product was filtered on silica gel (20 g) with ethyl acetate and then recrystallized from hexane, yielding 1.5 g (30%) of **13b**, mp 67–68 °C, as a rapidly polymerizing solid. Cold ethereal solutions of **13b** were stable: δ 3.70 (s, br, 4 H), 5.29 (t, $J \simeq 1$ Hz, 2 H), 5.80 (t, $J \simeq 1$ H, 2 H). At –40 °C: δ 3.72 (ABq, $J = 15.5$ Hz, $\Delta\nu = 20$ Hz, 4 H), 5.34 (m, 2 H), 5.84 (m, 2 H). $\Delta G^{\ddagger}$ was calculated[30] for T_c between 10 and 20 °C.[29] At 30 °C, with 0.5 molar equiv of Eu(fod)$_3$ added: δ 4.1 (ABq, $J = 15$ Hz, $\Delta\nu = 55$ Hz, 4 H), 5.34 (m, 2 H), 5.83 (m, 2 H); $\nu_{\max}$ (KBr) 1020, 920, 900 cm^{-1}; $\lambda_{\max}$ (ethanol) 244 nm (ϵ 6150); *m/e* 128 (M$^+$, base), 111, 85, 80, 79, 77.

Anal. Calcd for C_6H_8OS: C, 56.24; H, 6.99; S, 24.94. Found: C, 56.00; H, 6.25; S, 24.83.

An adduct with dimethyl acetylenedicarboxylate was prepared in toluene: dimethyl 3-thiabicyclo[4.3.0]nona-1(5),7-diene-7,8-dicarboxylate 3-oxide (**16b**), mp 145–146 °C (ethyl acetate); δ 3.20 (s, 4 H), 3.83 (s, 10 H; superimposed signals of six methyl protons and four five-membered-ring protons); $\nu_{\max}$ (KBr) 1700, 1280, 1060, 1030 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_5S$: C, 53.33; H, 5.22; S, 11.87. Found: C, 53.10; H, 5.16; S, 11.74.

3,4-Dimethylenethiolane 1,1-Dioxide (13c). Into a stirred solution of **13a** (3.2 g) in ether (100 mL) were added in small portions and at room temperature 12.0 g of solid 85% CPBA. After an additional hour, the solution was worked up as above and the crude product was filtered on silica gel (20 g) with ether–pentane 1:1 and recrystallized from ether–pentane to yield **13c** (1.3 g, 40%), mp 119 °C (when introduced onto the hot plate at a temperature close to the melting point); δ 3.93 (4 H), 5.23 (2 H), 5.78 (2 H; all singlets); $\nu_{\max}$ (KBr) 1305, 1125, 1110, 925, 880 cm^{-1}; $\lambda_{\max}$ (ethanol) 244 nm (ϵ 6680); *m/e* 144 (M$^+$), 80, 79 (base).

Sulfone **13c** was more stable in the solid state than sulfoxide **13b**, but it also polymerized after a few days. Cold solutions were stable for several weeks.

Anal. Calcd for $C_6H_8O_2S$: C, 50.00; H, 5.60; S, 22.21. Found: C, 50.11; H, 5.54; S, 22.47.

An adduct of **13c** with dimethyl acetylenedicarboxylate was prepared in methanol: dimethyl 3-thiabicyclo[4.3.0]nona-1(5),7-diene-7,8-dicarboxylate 3,3-dioxide (**16c**), mp 168–169 °C (methanol); δ 3.10 (s, 4 H), 3.63 (s, 10 H; superimposed signals of six methyl protons and four five-membered-ring protons); $\nu_{\max}$ (KBr) 1740, 1725, 1315, 1110 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}O_6S$: C, 50.35; H, 4.93; S, 11.18. Found: C, 50.24; H, 4.87; S, 11.28.

An adduct of **13c** with dimethyl azodicarboxylate was prepared in ether: dimethyl 8-thia-3,4-diazabicyclo[4.3.0]nona-1(6)-ene-3,4-dicarboxylate 8,8-dioxide (**19**), mp 150–151 °C (methanol); δ 3.81 (s, 6 H), 3.9–4.8 (m, 8 H); $\nu_{\max}$ (KBr) 1710, 1330, 1120 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O_6S$: C, 41.38; H, 4.86; N, 9.65; S, 11.03. Found: C, 41.65; H, 4.73; N, 9.69; S, 11.18.

3,4-Dimethyleneoxolane (14). To a solution of **1** (12 g) in ether (30 mL) was added a solution of potassium hydroxide (10 g) in dimethyl sulfoxide (45 mL) and water (15 mL). The mixture was stirred and warmed at 60 °C for 3 h. Standard workup and careful evaporation of the solvent at reduced pressure gave a residue that was distilled to yield pure **14**:[23] 1.7 g (35%), bp 50–55 °C (bath temperature) (20 torr); δ 4.40 (t, $J \simeq 2$ Hz, 4 H), 4.90 (t, $J \simeq 2$ Hz, 2 H), 5.41 (t, $J \simeq 2$ Hz, 2 H); $\nu_{\max}$ ($CHCl_3$) 1060, 910, 880 cm^{-1}; $\lambda_{\max}$ (isooctane) 245 nm (ϵ 9000).

An adduct of **14** with dimethyl acetylenedicarboxylate was prepared in methanol: dimethyl 8-oxabicyclo[4.3.0]nona-1(6),3-diene-3,4-dicarboxylate, mp 127–128 °C (methanol); δ 3.06 (s, 4 H), 3.80 (s, 6 H), 4.61 (s, 4 H).

Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.51; H, 5.83.

Preparation of 3,4-Dimethylenepyrrolidines (15). To a solution of **1** (1.2 g, 0.05 mol) in acetonitrile (30 mL), cooled to –15 °C, was added the desired secondary amine (0.15 mol). The solution was stirred for 1 h in the cold and for another hour at room temperature. A precipitate of a hydrobromide of the amine was filtered and water was added to the filtrate which was then extracted three times with 50 mL portions of 1 N hydrochloric acid. The combined acid solutions were extracted with ether, cooled in ice, made alkaline with 1 N sodium hydroxide, and extracted with ether once again. This last ether extract was washed with ice–water and then dried (potassium carbonate). The pyrrolidines obtained by evaporation of the ether were purified by crystallization or by chromatography and distillation.

1-Methyl-3,4-dimethylenepyrrolidine (**15a**):[24b] bp 60 °C (25 torr); yield 60%. Adduct with *N*-phenylmaleimide (prepared in benzene): 11-methyl-4,6-dioxo-5-phenyl-5,11-diazatricyclo[7.3.0.0^{3,7}]dodeca-1(9)-ene, mp 109–110 °C (methanol).

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.33; H, 6.44; N, 9.89.

1-Isopropyl-3,4-dimethylenepyrrolidine (**15b**)[24b] was obtained in 57% yield after chromatography on silica gel (elution: ether–hexane 5:1) and characterized as its methiodide.[24b]

1-*tert*-Butyl-3,4-dimethylenepyrrolidine (**15c**)[24b] was obtained in 52% yield from chromatography (as for **15b**) and then distilled, bp 85 °C (20 torr).

1-Cyclohexyl-3,4-dimethylenepyrrolidine (**15d**) was obtained in 51% yield from chromatography (as for **15b**); δ 1.0–2.2 (m, 11 H), 3.38 (t, $J \simeq 2$ Hz, 4 H), 4.93 (t, $J \simeq 2$ Hz, 2 H), 5.38 (t, $J \simeq 2$ Hz, 2 H).

A methiodide was prepared from **15d**, as described:[24b] 1-cyclohexyl-1-methyl-3,4-dimethylenepyrrolidinium iodide, mp >280 °C (ethanol–ether); δ (Me_2SO-d_6) 1.0–2.2 (m, 11 H), 2.78 (s, 3 H), 4.41 (s, br, 4 H), 5.33 (s, br, 2 H), 5.86 (s, br, 2 H).

Anal. Calcd for $C_{13}H_{22}NI$: C, 48.89; H, 6.94; N, 4.39. Found: C, 48.60; H, 6.82; N, 4.15.

1-Phenyl-3,4-dimethylenepyrrolidine (**15e**)[24a] was obtained in 75% yield, mp 126–128 °C (by introducing a sample of **15e** onto the hot plate at a temperature close to the melting point).

An adduct with dimethyl acetylenedicarboxylate was prepared from **15e** in benzene: dimethyl 8-phenyl-8-azabicyclo[4.3.0]-nona-1(6),3-diene-3,4-dicarboxylate, mp 179–180 °C (methanol–benzene); δ 3.03 (s, 4 H), 3.80 (s, 6 H), 4.03 (s, 4 H), 6.4–7.4 (m, 5 H).

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.21; H, 6.12; N, 4.13.

3,3-Dimethyl-3-azoniabicyclo[3.2.0]hept-1(5)-ene Iodide (23). A solution of 1,1-dimethyl-3,4-dimethylenepyrrolidinium iodide[24a] (1 g; derived from **15a** and methyl iodide in ether) in absolute methanol (100 mL) was irradiated for 10 h, with nitrogen flowing through the solution. Ether was added to the residue obtained after evaporation of the methanol and the precipitated solid was rapidly filtered and purified by passage on silica gel (10 g) in absolute methanol. The very hygroscopic solid obtained was recrystallized from dichloromethane, yielding 478 mg (48%) of **23**: mp 152–153 °C; δ 2.91 (s, br, 4 H), 3.66 (s, 6 H), 4.66 (s, br, 4 H).

Anal. Calcd for $C_8H_{14}IN$: C, 38.25; H, 5.62; N, 5.57. Found: C, 38.19; H, 5.46; N, 5.57.

3-Methyl-3-azabicyclo[3.2.0]hept-1(5)-ene (24a). A solution of **15a** (1.3 g) in ether was extracted with chilled 0.1 N hydrochloric acid (100 mL), and distilled water (200 mL) was added to the acid extract, the final pH being between 2 and 3. This aqueous acid solution was irradiated for 30 h while a flow of nitrogen through the solution was maintained. The acid solution was extracted with ether, made alkaline with 1 N sodium hydroxide, and extracted with pentane. The dried pentane solution (potassium carbonate) was evaporated, yielding 780 mg (60%) of over 95% pure **24a**, as shown by GC and ^{1}H NMR. The free product deteriorated rapidly and could not be chromatographed or distilled. Aqueous acidic or dry organic solutions of **24a** were stable in the cold for long periods of time. A pure sample was obtained by GC separation at 130 °C: δ 2.50 (s, 3 H), 2.66 (s, 4 H), 3.40 (s, 4 H); *m/e* 109 (M^+), 108, 47 (base).

A methiodide was prepared from **24a** by reaction with methyl iodide in ether and was found identical (melting point and ^{1}H NMR) with **23** obtained by irradiation of the methiodide of **15a**.

A picrate was prepared from **24a** by reaction with picric acid in concentrated ethanolic solution: 3-methyl-3-azoniabicyclo-[3.2.0]hept-1(5)-ene picrate, mp 135–136 °C (ethanol); δ 2.86 (s, 4 H), 3.16 (d, *J* = 5 Hz, 3 H), 4.26 (br ABq, $J \simeq 14$ Hz, $\Delta\nu = 58$ Hz, 4 H), 8.80 (s, 2 H), proton on nitrogen not observed.

Anal. Calcd for $C_{13}H_{14}N_4O_7$: C, 46.16; H, 4.17; N, 16.56. Found: C, 46.23; H, 4.04; N, 16.69.

3-*tert*-Butyl-3-azabicyclo[3.2.0]hept-1(5)-ene (24b). A solution of **15c** (1.1 g) in ether was treated as described above and irradiated for 15 h, yielding 714 mg (65%) of over 95% pure **24b**. The product was kept in aqueous acid solution or in dry organic solvents, in the cold. A sample was purified by GC at 130 °C: δ 1.11 (s, 9 H), 2.73 (s, br, 4 H), 3.56 (s, br, 4 H).

A picrate was prepared from **24b** by reaction with picric acid in concentrated ethanolic solution: 3-*tert*-butyl-3-azoniabicyclo[3.2.0]hept-1(5)-ene picrate, mp 163–164 °C; δ 1.46 (s, 9 H), 2.83 (s, br, 4 H), 4.20 (s, br, 4 H), 8.80 (s, 2 H), proton on nitrogen not observed.

Anal. Calcd for $C_{16}H_{20}N_4O_7$: C, 50.52; H, 5.30; N, 14.74. Found: C, 50.42; H, 5.54; N, 14.90.

Dimethyl 4,5-Bis(bromomethyl)-1,2,3,6-tetrahydropyridazine-1,2-dicarboxylate (27). A solution of **1** (10 g) and dimethyl azodicarboxylate (10 g) in benzene (50 mL) was refluxed for 1 h. The crude material was chromatographed on silica gel (100 g; elution: pentane–ether 1:1) and then recrystallized from pentane–ether to yield 9.25 g (63%) of **27**, mp 115–116 °C; δ 3.80 (s, 6 H), 4.04 (AB q, $J \simeq 10$ Hz, $\Delta\nu = 19$ Hz, 4 H), 4.25 (AB q, $J \simeq 15$, $\Delta\nu = 48$ Hz, 4 H).

The diethyl ester corresponding to **27** has been likewise prepared from diethyl azodicarboxylate, mp 90–91 °C (ether–pentane).

Anal. Calcd for $C_{12}H_{18}Br_2N_2O_4$ (diethyl ester): C, 34.80; H, 4.38; N, 6.77. Found: C, 34.80; H, 4.42; N, 6.77.

Dimethyl 4,5-Dimethylenehexahydropyridazine-1,2-dicarboxylate (28). To a solution of **27** (9 g) in dry ether (200 mL) was added 5 g of zinc–copper couple and the mixture was stirred and refluxed for 2 h, with HMPT (10 mL) being added after the first hour. The crude product obtained upon filtration on Celite and standard workup was purified by chromatography on silica gel (100 g; elution: ether–hexane 2:3), yielding 3.8 g (72%) of liquid, unstable **28** which was kept in solution: δ 3.69 (s, 6 H), 4.16 (AB q, *J* = 14.5 Hz, 4 H), 4.90 (s, 2 H), 5.20 (s, 2 H); ν_{max} ($CHCl_3$) 1724, 1212, 910 cm^{-1}.

An adduct with dimethyl azodicarboxylate was prepared in benzene: tetramethyl 1,2,3,4,5,6,7,8-octahydropyridazino[4,5-*d*]pyridazine-2,3,6,7-tetracarboxylate (**30**), mp 170–171 °C (ether–hexane); δ 3.80 (s, 12 H), 3.95 (AB q, $J \simeq 16$ Hz, $\Delta\nu = 46$ Hz, 8 H); ν_{max} (KBr) 1720, 1710 cm^{-1}; *m/e* 372 (M^+, base), 341, 313, 225.

Anal. Calcd for $C_{14}H_{20}N_4O_8$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.40; H, 5.44; N, 15.02.

3,4-Dimethylenehexahydropyridazine (29). To a solution of **28** (2.2 g) in methanol (15 mL) was added a solution of potassium hydroxide (1.2 g) in water (10 mL) and the total was refluxed under argon for 4 h. Acidification to decarboxylate and then basification with 5 N sodium hydroxide and extraction with ether yielded a crude product that was distilled to yield 717 mg (62%) of **29**, bp 60 °C (1.5 torr). The compound is unstable and oxidizes rapidly in air, turning red-brown in color; δ 3.45 (s, br, 2 H, N–H, exchanging with D_2O), 3.5 (t, *J* = 3 Hz, 4 H), 4.7 (t, *J* = 3 Hz, 2 H), 5.1 (t, *J* = 3 Hz, 2 H).

Tricarbonyl[dimethyl η^4-4,5-dimethylenehexahydropyridazine-1,2-dicarboxylate]iron (31). To a solution of **28** (1.3 g) in toluene (50 mL), stirred and maintained at 60 °C under a nitrogen atmosphere, was added, portionwise, 12 g of diiron nonacarbonyl over a period of 1 h. The reaction mixture was then maintained under the same conditions for 48 h. The cooled mixture was filtered on Celite and the residue was chromatographed on silica gel (100 g; elution: ether–hexane 3:7), yielding after crystallization from hexane 1.2 g (57%) of **31**: mp 108–109 °C; δ (at 50 °C) 0.18 (m, 2 H), 1.71 (m, 2 H), 3.76 (s, 3 H), 3.83 (s, 3 H), 4.39 (s, br, 2 H), 4.51 (AB q, *J* = 16 Hz, $\Delta\nu = 69$ Hz, 2 H); ν_{max} (KBr) 2050, 1995, 1720 cm^{-1}; *m/e* 366 (M^+), 338, 310 (base), 282.

Anal. Calcd for $C_{13}H_{14}FeN_2O_7$: C, 42.65; H, 3.85. Found: C, 42.59; H, 3.84.

Tricarbonyl[methyl η^4-4,5-dimethylenehexahydropyridazine-1-carboxylate]iron (32). To a solution of **31** (0.6 g) in methanol (15 mL) was added a solution of potassium hydroxide (0.4 g) in water (15 mL) and the total was refluxed for 1 h under a nitrogen atmosphere. Water (100 mL) and ether (100 mL) were added to the cooled mixture and the water layer was saturated with potassium carbonate and extracted with ether. The crude product was chromatographed on silica gel (50 g; elution: hexane–ether 1:1) to yield, after crystallization from hexane, 0.4 g (80%) of **32**: mp 87–88 °C; δ 0.29 (t, two superimposed anti vinylic protons), 1.69 (d, *J* = 2.9 Hz) and 1.75 (d, *J* = 3.3 Hz; two syn vinylic protons), 3.72 (AB q, $J \simeq 15$ Hz, $\Delta\nu = 48$ Hz, 2 H), 3.81 (s, 3 H), 4.25 (s, br, N–H, exchanged with D_2O), 4.40 (AB q, $J \simeq 13$ Hz, $\Delta\nu = 53$ Hz); ν_{max} (KBr) 3250, 2045, 1985, 1960, 1660 cm^{-1}; *m/e* 280 (M^+ – CO), 253 (base), 224, 168.

Anal. Calcd for $C_{11}H_{12}FeN_2O_5$: C, 42.88; H, 3.93. Found: C, 42.96; H, 4.05.

Tricarbonyl(η^4-4,5-dimethylenehexahydropyridazine)iron (33). Saponification and workup of **31** were carried out as described for **32**, with a reflux time of 5 h. A nitrogen atmosphere was maintained during workup and over the final solution. The total yield of **33**, as determined on an aliquot from this solution, was 0.21 g (55%). Crystallization from water gave crystals of **33**: mp 61–62 °C; δ (CD_3OD) 0.36 (d, $J \simeq 3$ Hz, 2 H), 1.73 (d, $J \simeq 3$ Hz, 2 H), 3.77 (AB q, $J \simeq 15$ Hz, $\Delta\nu = 28$ Hz, 4 H); ν_{max} (KBr) 3300, 1995, 1975, 1960 cm^{-1}.

Anal. Calcd for $C_9H_{10}FeN_2O_3$: C, 43.23; H, 4.03. Found: C, 43.41; H, 4.15.

Tricarbonyl(η^4-4,5-dimethylene-1,4,5,6-tetrahydropyridazine)iron (34). The final worked-up ether solution of **33**, prepared from 0.9 g of **31** as described above, was exposed uncovered to the air atmosphere, at room temperature, for 15 min. The solution became yellow during this time. The solvent was then evaporated and the residue was chromatographed on silica gel (60 g, elution hexane–ether 3:2) to yield, after crystallization from hexane, 275 mg (45%) of **34**: mp 108–109 °C; δ 0.22 (d, *J* = 2.9 Hz) and 0.40 (d, *J* = 2.6 Hz; two anti vinylic protons), 1.70 (two partially overlapping doublets, $J_1 = 2.9$ Hz, $J_2 = 2.6$ Hz; two syn vinylic protons), 3.92 (AB q, $J \simeq 14$ Hz, $\Delta\nu = 50$ Hz, 2 H), 6.25 (br, N–H, exchanged with D_2O), 7.12 (s, 1 H); ν_{max} (KBr) 3280, 2040, 1980, 1950 cm^{-1}; *m/e* 248 (M^+), 220, 192, 164, 137 (base), 108.

Anal. Calcd for $C_9H_8FeN_2O_3$: C, 43.59; H, 3.25. Found: C, 43.31; H, 3.13.

Dimethyl 4,5-Bis(bromomethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (35). A solution of **1** (18 g) and dimethyl acetylenedicarboxylate (10.8 g) in diglyme (90 mL) was refluxed for 90 min. Standard workup yielded 30 g of a crude oily mixture that was chromatographed on silica gel (400 g). Elution with up to 30% ether in hexane yielded some unidentified components. Further elution with hexane–ether 3:2 yielded a solid product that was recrystallized from hexane to give 15.0 g (52%) of **35**: mp 75–76 °C; δ 3.22 (s, 4 H), 3.82 (s, 6 H), 4.08 (s, 4 H); ν_{max} (KBr) 1724, 1292, 1266, 1239, 1205, 1047 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}Br_2O_4$: C, 37.72; H, 3.69; Br, 41.83. Found: C, 37.90; H, 3.75; Br, 41.90.

Dimethyl 4,5-Dimethylenecyclohexene-1,2-dicarboxylate (36). Dibromide **35** (5.4 g) was stirred and refluxed in ether (150 mL) for 1 h in the presence of zinc–copper couple (2.2 g). Monitoring by TLC then showed the absence of any starting material. (If the reaction is reluctant to start, 10% HMPT may be added.) Filtering, washing with ammonium chloride and with sodium chloride solutions, drying, and evaporating the solvent yielded 3.0 g (95%) of crude **36**, which showed on NMR only such peaks that were compatible with the proposed structure: δ 3.27 (s, 4 H), 3.78 (s, 6 H), 4.92 (s, br, 2 H), 5.27 (s, br, 2 H); $\nu_{\max}$ (CCl_4) 1730, 1658, 1266, 1244, 910 cm^{-1}.

An adduct of **36** with sulfur dioxide was prepared by bubbling an excess of the gas into the crude ether solution, decanting the solution from the zinc, and allowing the stoppered solution to stand overnight at room temperature. The sulfone obtained by evaporation of the solvent and recrystallization from ethanol was identical with **16c**, prepared from **13c**, mp 169–170 °C.

Tetramethyl 1,4,5,8-Tetrahydronaphthalene-2,3,6,7-tetracarboxylate (37). An adduct with dimethyl acetylenedicarboxylate (1.9 g) was prepared from the total amount of crude **36**, obtained as described above from 5.4 g of **35**, by refluxing for 0.5 h in diglyme. Upon addition of some water and cooling, quite pure **37** precipitated (3.75 g, 73% from **35**). Recrystallization from ethanol yielded pure **37**, mp 191–192 °C; δ 2.95 (s, 8 H), 3.82 (s, 12 H); $\nu_{\max}$ (KBr) 1715, 1270, 1060 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}O_8$: C, 59.34; H, 5.53. Found: C, 59.25; H, 5.49.

Hexacarbonyl[μ-[η^3:η^3-2,3-dimethylenetetramethylene)]diiron(*Fe-Fe*) (38). Tetrabromide **2** (4 g) was stirred and warmed to 60 °C in hexane (50 mL), under nitrogen, and 20 g of diiron nonacarbonyl was added portionwise during 3 h. After an additional reflux time of 4 h, the mixture was filtered and evaporated to dryness. The residue was filtered with pentane on silica gel (50 g) and the red product was recrystallized from hexane, yielding 720 mg (20%) of **38**: mp 88–89 °C (lit.[40] 88 °C); δ 1.50 (s, 4 H), 1.56 (s, 4 H).

***trans*- and *cis*-Hexacarbonyl{μ-[η^4:η^4-(1,4-cyclohexanediylidene-1,3-propanediyl-2-ylidene)]}diiron (39 and 40).** A solution of **1** (16 g) in hexane (280 mL) was treated as above, using 59 g of diiron nonacarbonyl. Chromatography on silica gel (800 g, using dry pentane as eluent) yielded three incompletely separated main fractions. Complete separation of pure components was achieved by repeated chromatography of these fractions on 100-fold quantities of silica gel. By order of elution, the complexes **39** (1.1 g, 7.5%), **38** (2.5 g, 10%), and **40** (0.3 g, 2%) were thus obtained.

Complex **39**: mp 210–211 °C (hexane); δ 1.85 (s, 4 H), 1.91 (s, 8 H), 2.31 (s, 4 H); ^{13}C NMR: δ ($CDCl_3$) 37.5, 49.1, 96.1, 100.4 (carbonyl carbon shifts were not recorded); $\nu_{\max}$ (KBr) 2045, 1985, 1970, 1960 cm^{-1}; $\lambda_{\max}$ (isooctane) 275 nm (sh; ϵ 2480); *m/e* 440 (M^+), 300 (base); cell units, see text.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 49.09; H, 3.77.

Complex **40**: mp 203–204 °C (hexane); δ 1.82 (s, 4 H), 1.87 (s, 8 H), 2.26 (s, 4 H); $\nu_{\max}$ (KBr) 2055, 2000, 1987 (sh), 1980, 1973, 1964; $\lambda_{\max}$ (isooctane) 275 nm (sh, ϵ 2200); *m/e* 440 (M^+), 270 (base).

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 49.02; H, 3.60.

***trans*-{μ-[η^4:η^4-1,4-Bis(1-methylethenyl)-1,3-cyclohexadiene]}hexacarbonyldiiron (41a) and *trans*-{μ-[η^4:η^4-1,4-Bis(1-methylethenyl)-1,4-cyclohexadiene]}hexacarbonyldiiron (42a).** Solid complex **39** (210 mg) was dissolved during 10 min, with stirring, in concentrated sulfuric acid cooled to −10 °C. Standard workup yielded a mixture of two components (190 mg, 95%) which were separated by chromatography on silica gel (20 g) with dry pentane as eluent.

Complex **41a**: mp 208–209 °C (hexane; 83.9 mg, 40%); δ 0.30 (d, J = 2.5 Hz, 2 H, anti methene protons), 1.46 (s, 2 H; ring vinylic protons), 1.77 (d, J = 2.5 Hz, 2 H, syn methene protons), 2.19 (s, 6 H, methyls), 3.00 (AB q, J = 10 Hz, $\Delta\nu$ = 15 Hz, 4 H, ring methylenes); $\nu_{\max}$ (KBr) 2030, 1960 (sh), 1950 cm^{-1}; $\lambda_{\max}$ (isooctane) 265 sh, 330 nm (ϵ 14 000, 8700); *m/e* 440 (M^+), 298, 270 (base).

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 48.93; H, 3.58.

Complex **42a**: mp 170–171 °C (hexane; 86.3 mg, 41%); δ 0.13 (d, J = 2.5 Hz, 2 H, anti methene protons), 1.21 (dd, J_1 = 2.5 Hz, J_2 = 6.5 Hz, 2 H, ring vinylic protons), 1.71 (d, J = 2.5 Hz, 2 H, syn methene protons), 2.19 (s, 6 H, methyls), 3.27 (d AB q, J_{AB} = 20 Hz, J_1 = 2.5 Hz, J_2 = 6.5 Hz, $\Delta\nu$ = 27 Hz, 4 H, ring methylenes); $\lambda_{\max}$ (KBr) 2030, 1976, 1951 cm^{-1}; $\lambda_{\max}$ (isooctane) 300 nm (ϵ 6350); *m/e* 440 (M^+), 298 (base), 270.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 49.02; H, 3.51.

***cis*-{μ-[η^4:η^4-1,4-Bis(methylethenyl)-1,3-cyclohexadiene]}hexacarbonyldiiron (41b) and *cis*-{μ-[η^4:η^4-1,4-Bis(1-methylethenyl)-1,4-cyclohexadiene]}hexacarbonyldiiron (42b).** Solid complex **40** (320 mg) was treated with concentrated sulfuric acid as described for **39**. Chromatography on silica gel separated the two derived isomers.

Complex **41b**: mp 162–163 °C (hexane; 119 mg, 37%); δ 0.14 (d, J = 2.5 Hz, 2 H, anti methene protons), 1.90 (d, J = 2.5 Hz, 2 H, syn methene protons), 1.94 (s, 2 H, ring vinylic protons), 2.31 (s, 6 H, methyls), 3.16 (s, 4 H, ring methylenes); $\nu_{\max}$ (KBr) 2045, 2020, 1980, 1965, 1945, 1940 cm^{-1}; $\lambda_{\max}$ (isooctane) 272, 330 (sh) nm (ϵ 12 200, 6060); *m/e* 440 (M^+), 298 (base), 270.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 48.95; H, 3.53.

Complex **42b**: mp 168–169 °C (hexane; 156 mg, 46%); δ 0.01 (d, J = 2 Hz, 2 H, anti methene protons), 1.21 (dd, apparent triplet, br, J_1 = 7 Hz, J_2 = 8 Hz, 2 H, ring vinylic protons), 1.71 (d, J = 2 Hz, 2 H, syn methene protons), 2.26 (s, 6 H, methyls), 2.35 and 3.65 (d AB q, J_{AB} = 16 Hz, J_1 = 7 Hz, J_2 = 8 Hz, 4 H, ring methylenes); $\nu_{\max}$ (KBr) 2045, 2035, 1970, 1955, 1945 cm^{-1}; $\lambda_{\max}$ (isooctane) 303 nm (ϵ 6700); *m/e* 440 (M^+), 298 (base), 270.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$: C, 49.13; H, 3.67. Found: C, 49.10; H, 3.55.

Oxidation of Complex 42a. To a solution of **42a** (160 mg) in methanol (130 mL) was added, with stirring, a fresh solution of cerric ammonium nitrate (1.170 g) in methanol (50 mL). After the induced gas evolution had stopped, the reaction mixture was filtered on Celite and evaporated at reduced pressure. The residue showed two peaks on GC, in a ratio of ca. 8:1, and was separated by preparative GC to yield diisopropenylbenzene as the major constituent, identical with an authentic sample prepared according to a described procedure,[46] and 1,4-diisopropenyl-1,4-cyclohexadiene (6 mg, 10%): mp 115 °C (lit.[47] mp 117–117.5 °C); high-resolution mass spectrum, *m/e* 160.1264 (M^+, calcd for $C_{12}H_{16}$, 160.1252), 145.1020 ($C_{11}H_{13}^+$, base), 130.0863 ($C_{10}H_{11}^+$), 117.0665 ($C_9H_9^+$), 105.6676 ($C_8H_9^+$).

Registry No. 1, 18214-55-6; **2**, 30432-16-7; **4**, 72524-93-7; **5a** (n = 1), 72524-94-8; **5a** (n = 2), 72524-95-9; **5a** (n = 3), 72524-96-0; **5b** (n = 2), 16714-60-6; **5b** (n = 3), 72524-97-1; **5b** (n = 4), 72524-98-2; **5c** (n = 2), 72524-99-3; **5c** (n = 3), 72525-00-9; **5d** (n = 3), 72525-01-0; **5e** (n = 2), 72525-02-1; **5e** (n = 3), 72525-03-2; **5f** (n = 1), 72525-04-3; **6**, 27567-69-7; **7** (n = 2), 72525-05-4; **7** (n = 3), 72558-79-3; **8**, 66341-50-2; **9**, 72525-06-5; **10**, 72525-07-6; **11**, 72525-08-7; **12a**, 50521-46-5; **12b**, 50521-47-6; **12c**, 17637-48-8; **12d**, 34875-84-8; **12e**, 19869-23-9; **12f**, 50521-52-3; **12g**, 50521-53-4; **12h**, 50521-50-1; **13a**, 50288-90-9; **13b**, 50288-92-1; **13c**, 50288-93-2; 14, 50521-40-9; **15a**, 50521-42-1; **15b**, 50586-31-7; **15b** methiodide, 50586-37-3; **15c**, 50586-32-8; **15d**, 72525-09-8; **15d** methiodide, 72525-10-1; **15e**, 50521-41-0; **16a**, 50288-91-0; **16b**, 50288-96-5; **16c**, 50288-97-6; **17**, 50288-94-3; **18**, 50288-95-4; **19**, 50289-00-4; **23**, 72525-11-2; **24a**, 72525-12-3; **24a** picrate, 72525-13-4; **24b**, 72525-14-5; **24b** picrate, 72525-15-6; **27**, 72525-16-7; **27** diethyl ester, 72525-17-8; **28**, 72525-18-9; **29**, 72525-19-0; **30**, 72525-20-3; **31**, 72525-89-4; **32**, 72525-90-7; **33**, 72525-91-8; **34**, 72525-92-9; **35**, 50521-55-6; **36**, 50288-98-7; **37**, 72525-21-4; **38**, 72525-93-0; **39**, 57031-26-2; **40**, 56977-56-1; **41a**, 72597-28-5; **41b**, 72581-29-4; **42a**, 72581-30-7; **42b**, 72597-29-6; sodium *p*-toluenesulfinate, 824-79-3; *N*-phenylmaleimide, 941-69-5; tricyclo[10.4.0.0^{4,9}]hexadeca-1(12),4(9)-diene-6,7:14,15-bis(*N*-phenyldicarboximide), 72525-22-5; vinyl chloride, 75-01-4; 4,5-bis(2-propenyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide), 72525-23-6; 1,2-bis[4-(2-propenyl)-1,2-(*N*-phenyldicarboximido)-4-cyclohexen-5-yl]ethane, 72525-24-7; ethynyl bromide, 593-61-3; 4,5-bis(2-propynyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide), 72525-25-8; 4,5-bis(methoxymethyl)-4-cyclohexene-1,2-(*N*-phenyldicarboximide), 50521-44-3; maleic anhydride, 108-31-6; 4,5-bis(methoxymethyl)-4-cyclohexene-1,2-dicarboxylic anhydride, 50521-45-4; dimethyl acetylenedicarboxylate, 762-42-5; benzoyl chloride, 98-88-4; 2-(acetoxymethyl)-3-(bromomethyl)-1,3-butadiene, 72525-26-9; 2,7-bis(acetoxymethyl)-3,6-dimethylene-1,7-octadiene, 72525-27-0; dimethyl azodicarboxylate, 2446-84-6; dimethyl 8-oxabicyclo[4.3.0]nona-1-(6),3-diene-3,4-dicarboxylate, 50940-16-4; methylamine, 74-89-5;

isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; cyclohexylamine, 108-91-8; phenylamine, 62-53-3; dimethyl 8-phenyl-8-azabicyclo[4.3.0]nona-1(16),3-diene-3,4-dicarboxylate, 50940-17-5; 1,1-dimethyl-3,4-dimethylenepyrrolidinium iodide, 50586-35-1; diethyl azodicarboxylate, 1972-28-7; diiron nonacarbonyl, 15321-51-4; sulfur dioxide, 7446-09-5; 1,4-diisopropenylbenzene, 1605-18-1; 1,4-diisopropenyl-1,4-cyclohexadiene, 56892-50-3; 11-methyl-4,6-dioxo-5-phenyl-5,11-diazatricyclo[7.3.0.0^{3,7}]dodeca-1(9)-ene, 50521-58-9.

Ring Transformations and Amination in Reactions of 3-Halogeno-5-phenyl-1,2,4-triazines with Potassium Amide in Liquid Ammonia[1-3]

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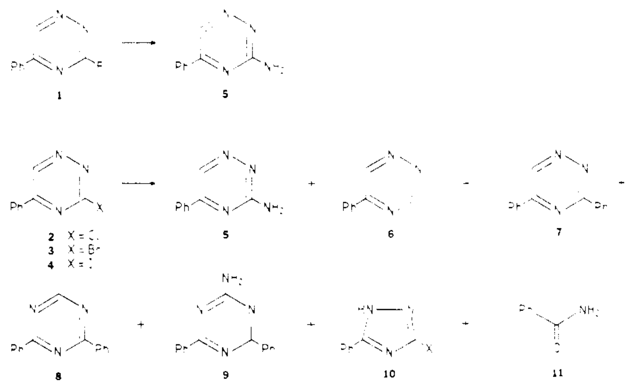
The reactions of 3-X-5-phenyl-1,2,4-triazines (X = fluoro, chloro, bromo, iodo) toward potassium amide/liquid ammonia were studied. Whereas the 3-fluoro compound gives only the 3-amino derivative, the 3-chloro, 3-bromo, and 3-iodo compounds yield a complex mixture containing, besides 3-amino-5-phenyl-1,2,4-triazine and 5-phenyl-1,2,4-triazine, ring-transformation products, i.e., 3,5-diphenyl-1,2,4-triazine, 2,4-diphenyl-1,3,5-triazine, 6-amino-2,4-diphenyl-1,3,5-triazine, and 3-X-5-phenyl-1,2,4-triazole. Evidence is found that in the ring transformation of 3-X-5-phenyl-1,2,4-triazines into 2,4-diphenyl-1,3,5-triazines, benzamidine must be an intermediate. The mechanisms of the amination and ring transformation are extensively discussed.

1. Introduction

Recent investigations of the amination of 3-(methylthio)-1,2,4-triazine with potassium amide in liquid ammonia have shown[4] that this conversion occurs to a great extent according to a mechanism involving ring opening [S_N(ANRORC) mechanism[5]]. This mechanism involves a primary addition of the amide ion to the π-deficient C-5 position of the 1,2,4-triazine ring and ring opening into an open-chain intermediate, which undergoes recyclization into the corresponding 3-amino compound. ^1H and ^{13}C NMR spectroscopic studies[1] of solutions of 1,2,4-triazine and some of its derivatives in liquid ammonia confirm that the 1,2,4-triazine ring forms exclusively a σ adduct at C-5. These studies induced us to investigate in more detail the behavior of 5- and/or 6-substituted 1,2,4-triazines with a C-3 group having considerable leaving character with respect to anionic nucleophiles.

In the present paper we report the results of an investigation of the reactions of 3-halogeno-5-phenyl-1,2,4-triazines with potassium amide in liquid ammonia. These compounds are of particular interest since the presence of the phenyl group at C-5 can retard or at least prevent addition of the amide ion to C-5, facilitating the attack of a nucleophile at C-3 of the 1,2,4-triazine ring.

Scheme I



2. Results

The hitherto unknown compounds 3-fluoro- (1), 3-chloro- (2), 3-bromo- (3), and 3-iodo-5-phenyl-1,2,4-triazine (4) were synthesized according to standard procedures. The preparations are extensively described in the Experimental Section. It was found that treatment of 1 with potassium amide/liquid ammonia at -75 °C for 5 min gave nearly exclusively 3-amino-5-phenyl-1,2,4-triazine (5) (Scheme I). Only a trace of an unidentifiable tar is obtained. In contrast, treatment of the compounds 2–4 with potassium amide at -33 °C for 15 min gave complex reaction mixtures. We were able to identify in these mixtures the presence of the 3-amino compound 5, the dehalogenated product 5-phenyl-1,2,4-triazine (6), and the ring transformation products 3,5-diphenyl-1,2,4-triazine (7), 2,4-diphenyl-1,3,5-triazine (8), 6-amino-2,4-diphenyl-1,3,5-triazine (9), 3-X-5-phenyl-1,2,4-triazole (10; X =

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[1] Part 24 on NMR investigations of σ adducts of heterocyclic systems with nucleophiles. For part 23, see: J. Breuker and H. C. van der Plas, *J. Org. Chem.*, 44, 4677 (1979).

[2] Part 42 on ring transformations of heterocyclic halogeno compounds with nucleophiles. For previous paper, see: A. Nagel, H. C. van der Plas, G. Geurtsen, and A. van der Kuilen, *J. Heterocycl. Chem.*, 16, 309 (1979).

[3] Part 26 on the S_N(ANRORC) mechanism. For part 25, see: J. Breuker and H. C. van der Plas, *J. Org. Chem.*, 44, 4677 (1979). For part 24 see: H. C. van der Plas, *Acc. Chem. Res.*, 11, 462 (1978).

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[5] For a recent review on the occurrence of the S_N(ANRORC) mechanism in nucleophilic substitution, see: H. C. van der Plas, *Acc. Chem. Res.*, 11, 462 (1978).

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