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PREPARATION OF DIADDUCTS FROM DIENES AND DIHALOCARBENES. A GENERAL SONOCHEMICAL METHOD.

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Abstract: Diadducts were formed in excellent yields from reactions of dienes with chloroform or bromoform, powdered sodium hydroxide and benzyltriethylammonium chloride as catalyst using ultrasound.

Addition of dihalocarbenes to dienes may occur at one or both of the double bonds, furnishing the cyclopropane monoadducts and diadducts, respectively.[1] The ratio between the adducts depends on the particular dihalocarbene employed and the way it is generated. Among the methods used so far it seems that phase- transfer conditions generally give better yields of diadducts. Dichlorocarbene generated in this way requires in many cases a considerably higher than 2:1 ratio of chloroform to diene in order to obtain acceptable yields of diadducts. This requirement seems even more important for similar additions of dibromocarbene; however, irrespective of the method of generation, with few exceptions the monoaddition product has been reported to be the major product.[1] This is exemplified by

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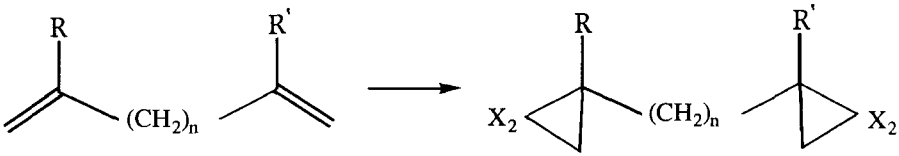
the addition of dibromocarbene to 1,3-butadiene yielding only a small amount of the diadduct, while a similar addition to 2,4-dimethyl-2,4-hexadiene produced the diadduct in excellent yield.[2] A general method for the preparation of diadducts should be of interest, since they are attractive as starting material for the preparation of bisallenes[3] and fulvenes.[4]

A new method by Brinker and Xu, which generates dibromocarbene from bromoform and powdered sodium hydroxide under ultrasonic conditions, was brought to our attention.[5] When this method was applied to isoprene we obtained the corresponding diadduct as a mixture of two diastereoisomers in 82% yield. Only the monoadduct has been reported previously as product from reactions of isoprene and dibromocarbene. This encouraged us to react a few dienes under the new conditions in order to obtain an indication of its scope. The results with some open-chain dienes **1** are presented in the Table.

The reactions were carried out with a 3:1 ratio of haloform to diene, and with reaction times of 90 min and 60 min for the reactions with bromoform and chloroform, respectively. For the reactions with bromoform it was found advantageous with respect to yields to add the bromoform and base in two equal portions twice during the reaction (see experimental). In some cases under these conditions small amounts of the corresponding monoadducts were formed as well. The products were characterized spectroscopically and by comparison with authentic samples. The diadducts consisted of mixtures of diastereoisomers, but from symmetrical dienes the meso compounds predominated in all cases.

Addition of dibromocarbene to 1,4-cyclohexadiene by the present method gave the *anti* tricyclic compound **3**[10] in 55% yield. Similarly, the reaction of tetramethylallene yielded 35% of **4**, the monoadduct **5** being still the major product. Only a low



1 2

FIG. 1

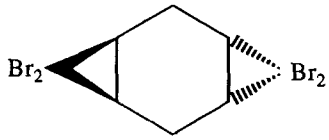
Table

Yields of diadducts **2** from dienes **1**

n	R	R'	X	Yield %	Litt. yield %	Ref.
0	H	H	Br	81	9[a]	2
0	H	Me	Br	82	0	2,6
0	Me	Me	Br	98	32[b]	2
0	Me	Me	Cl	93	75[c]	7
2	H	H	Br	82	38[d]	8
2	Me	Me	Br	81	61[e]	9
2	Me	Me	Cl	71	75[c]	7

Molar ratio $CHBr_3$-diene: a) 3; b)2.5; c) 5; d) not given; e) 2
The yields are isolated yields of mixtures of diastereoisomers, containing no more than 5 % of other compounds as estimated by ^{1}H-NMR.

yield (10%) of the spiropentane **4** had been obtained previously.[11] Flash chromatography of the product mixture resulted in partial isomerization of the monoadduct **5** to 2,5-dimethyl-3,4-dibromohexadiene (**6**). The isomerization could be completed by leaving the products absorbed onto silica at room temperature overnight. This isomerization has been reported earlier to take place in polar solvents at 100-140 °C with other *gem*-dibromo-1-alkylidenecyclopropanes.[12] Tetraphenylallene was quite unreactive towards dibromocarbene generated under the present conditions.



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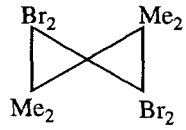

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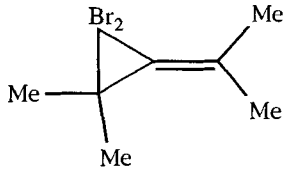
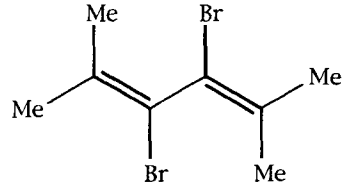


5



6

FIG. 2

Our results show that the present method is preferred for the preparation of diadducts from dienes and dihalocarbenes. It requires only a small excess of haloform and relatively short reaction time. Experiments with isoprene and bromoform revealed that with a molar ratio $CHBr_3$-diene of 2.1 and 90 min reaction time the diadduct was still the major product, but with a molar ratio of 1 and the same reaction conditions the monoadduct, 2,2-dibromo-1-methyl-1-vinylcyclopropane, was formed almost exclusively. Similar results were obtained with 2,5-dimethyl-1,5-hexadiene and bromoform. Hence, the method is certainly useful for preparing monoadducts provided equimolar amounts of diene and haloform are used.

Experimental:

General procedure

A solution of the diene (25 mmol), TEBA (0.5 mmol, 114 mg), and haloform (38 mmol) in methylene chloride (25 ml) was immersed

in the water bath of an ultrasonic cleaner. The flask was positioned *ca.* 0.5 cm above the bottom of the bath, and the level of water was adjusted to that of the solvent level inside the flask. After adding powdered sodium hydroxide (5.0 g, 125 mmol) the mixture was treated with ultrasound for 45 min. More haloform (38 mmol) and sodium hydroxide (5.0 g, 125 mmol) were then added, and the treatment with ultrasound continued for another 45 minutes. Approximately 3 g of Celite was added, and the reaction mixture was filtered with suction through a 1 cm bed of Celite.
The collected solid was washed thoroughly with methylene chloride, and the combined extracts were concentrated under reduced pressure. The final purification was done by flash chromatography (SiO_2, petrol. ether).

2,2,2',2'- Tetrabromo-1,1'-bicyclopropyl (**2**, n = 0, R = H, R'= H, X = Br)[2] was obtained in 81% yield from 1,3-butadiene as a solid mixture of diastereoisomers in a 1:1 ratio. MS (70 eV) *m/z* 315 (M^+-Br), 156/158 (100%), 78, 77, 51; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.42-1.60 (m, 2 H), 1.62-1.83 (m, 2 H), 1.84-2.06 (m, 2 H);
Isomer 1: ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 26.4, 29.7, 34.1.
Isomer 2: ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 25.7, 29.1, 33.8.

2,2,2',2'- Tetrabromo-1-methyl-1,1'-bicyclopropyl (**2**, n = 0, R = Me, R'= H, X = Br) was obtained in 82% yield from isoprene as a liquid mixture of diastereoisomers in a 2:1 ratio, which we were unable to separate. The spectra are recorded on the mixture. MS (70 eV) *m/z* 408 (M^+), 237/239/241, 171/173, 170/172, 92, 91 (100 %); HRMS: Found: 407.7403. Calc. for $C_7H_8Br_4$: 407.7362.
Major isomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30 (t, *J*=8.2 Hz, 1 H), 1.46 (d, *J*=8.5 Hz, 1 H), 1.48 (d, *J*=8.5 Hz, 1 H), 1.65 (s, 3 H), 1.87 (dd, *J*=8.3 Hz and 10.6 Hz, 1 H), 2.03-2.08 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.7, 25.3, 29.2, 30.9 , 32.3, 33.7, 36.9.
Minor isomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26 (s, 3 H), 1.69-1.74 (m, 2 H), 1.92 (dd, *J*=7.8 Hz and 11.2 Hz, 1 H), 2.03-2.08 (m, 1 H), 2.29 (dd, *J*=8.6 Hz and 11.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.8, 27.6, 28.0, 28.7, 35.2, 36.1, 39.9.

2,2,2',2'- Tetrabromo-1,1'-dimethyl-1,1'-bicyclopropyl (**2**, n = 0, R = Me, R'= Me, X = Br)[2] was obtained in 98% yield from 2,3-dimethyl-1,3-butadiene. mp. 92.5-95.5 °C (lit.[2] mp. 96-99 °C); MS (70 eV) *m/z* 422 (M^+), 172/174 (100 %), 105, 93, 51; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.50 (s, 4 H), 1.63 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.2, 34.4, 34.9, 35.8.

2,2,2',2'- Tetrachloro-1,1'-dimethyl-1,1'-bicyclopropyl (**2**, n = 0, R = Me, R' = Me, X = Cl)[7] was obtained in 93% yield from 2,3-dimethyl-1,3-butadiene as a liquid. MS (70 eV) *m/z* 246 (M^+), 163/165/167, 127(100 %)/129, 91, 77; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29 (s, 4 H), 1.57 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.5, 33.0, 34.4, 64.7.

1,2-Bis(2,2-dibromocyclopropyl)ethane (**2**, n = 2, R = H, R' = H, X = Br)[2] was obtained in 82% yield from 1,5-hexadiene as a liquid mixture of diastereoisomers in a 1:1 ratio. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15-1.35 (m, 2 H), 1.50-1.90 (m, 8 H)
Isomer 1: ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.7, 30.7, 31.2.
Isomer 2: ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.4, 30.8, 31.4.

1,2-Bis(2,2-dibromo-1-methylcyclopropyl)ethane (**2**, n = 2, R = Me, R' = Me, X = Br)[2] was obtained in 81% yield from 2,5-dimethyl-1,5-hexadiene as a solid mixture of diastereoisomers in a 1:1 ratio, from which the meso isomer could be isolated by recrystallisation from methanol.
Meso-**2**: mp. 121-123 °C (lit.[2] mp. 121-122 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.36 (s, 6 H), 1.39-1.45 (m, 2 H), 1.47-1.54 (m, 2 H), 1.62-1.73 (m, 2 H), 1.95-2.10 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.5, 29.3, 35.0, 35.4, 38.9.
Rac.-**2**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (s, 6 H), 1.41 (s, 4 H), 1.64-1.94 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.6, 29.4, 34.5, 35.2, 39.1.

1,2-Bis(2,2-dichloro-1-methylcyclopropyl)ethane (**2**, n = 2, R = Me, R' = Me, X = Cl)[7] was obtained in 71% yield from 2,5-dimethyl-1,5-hexadiene as a mixture of diastereoisomers, from which the meso isomer could be isolated by recrystallisation from methanol.
Meso-**2**: mp. 77-79 °C (lit.[7] mp. 82 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.21 (d, *J*=7.0 Hz, 2H), 1.26 (d, *J*=7.0 Hz, 2 H), 1.31 (s, 6 H), 1.53-1.69 (m, 2 H), 1.88-1.99 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.2, 30.2, 32.9, 33.7, 67.7.

Rac.-**2**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20 (s, 4 H), 1.30 (s, 6 H), 1.71-1.81 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.3, 30.3, 32.6, 33.3, 67.7.

anti-*4,4,8,8-tetrabromotricyclo[5.1.0.0^{3,5}]octane* (**3**)[10] was obtained in 55 % yield from 1,4-cyclohexadiene as a solid. mp. 205-207 °C. (lit.[10] mp. 207-209 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.69-1.76 (m, 4 H), 2.04-2.12 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 16.3, 24.4, 36.1.

1,1,4,4-Tetrabromo-2,2,5,5-tetramethylspiro[2.2]pentane (**4**).[13] was obtained in 35 % yield from tetramethylallene, admixed with the monoadduct **5** and the diene **6**. The spiropentane **4** could be isolated by recrystallisation from methanol. mp. 213-215 °C (dec.) (lit.[13] mp. 216 °C (dec.)). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.40 (s, 6 H), 1.52 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 22.9, 23.9, 36.0, 45.2, 47.3; MS (70 eV) *m/z* 357(M^+-Br), 279, 199, 198, 119 (100 %).

1,1-Dibromo-2-isopropylidene-3,3-dimethylcyclopropane (**5**).[13] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.40 (s, 6 H), 1.80 (s, 3 H), 1.93 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 20.6, 21.6, 24.4, 32.4, 35.7, 129.3, 132.4; MS (70 eV) *m/z* 266 (M^+), 187/189, 108 (100 %), 107, 93.

3,4-Dibromo-2,5-dimethyl-2,4-hexadiene (**6**).[14] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.72 (s, 6 H), 1.89 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 21.4, 24.2, 116.3, 136.6; MS (70 eV) *m/z* 266 (M^+), 187/189, 108 (100 %), 107, 93.

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