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Chemistry of *gem*-Dihalocyclopropanes. XX. The Effect of Methyl and Phenyl Substituents on the Vinylcyclopropylidene–Cyclopentenylidene Rearrangement

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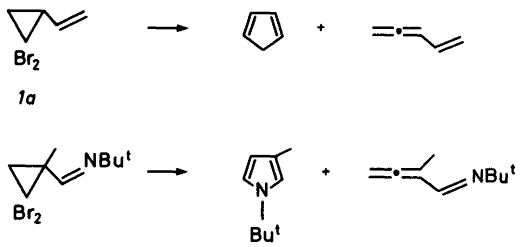
Reactions of *gem*-dibromocyclopropanes of the general structure *1* with methyllithium have been studied. In most cases cyclopentadienes and/or vinylallenes are the products formed. The results obtained give evidence of a profound substituent effect on the carbene-carbene rearrangement leading to cyclopentadienes. We believe the effect is essentially steric in origin. The results support the mechanism proposed for the rearrangement.

Reactions of the readily avilable *gem*-dibromocyclopropanes with alkyllithium is a much used method for preparation of allenes and cumulenes.[1] However, depending on the substituents, other reactions than ring-opening to allenes are frequently encountered. Some years ago one of us discovered that 1,1-dibromo-2-vinylcyclopropane (*1a*) reacted with methyllithium at −78 °C to yield mainly cyclopentadiene besides vinylallene[2] (Scheme 1). It was proposed that cyclopentadiene resulted from a vinylcyclopropylidene-cyclopentenylidene rearrangement, and subsequent studies support this notion.[3–5] The effect of substituents on the rearrangement is not known, but according to the suggested mechanism, steric interactions should be important. Furthermore, MINDO calculations indicate that the rearrangement is influenced by electronic effects as well.[6] It should also be mentioned that 2,2-dibromocyclopropanimines react with methyllithium to the corresponding pyrrols, among other products, apparently by a similar rearrangement (Scheme 1).[7,8]



Scheme 1.

We have initiated a study with the purpose of obtaining information about how substituents affect the carbene-carbene rearrangement, anticipating the results would throw some light on the mechanism and on the scope of the reaction as well. This paper reports on the reactions of a number of alkyl- and phenyl-substituted 1,1-dibromo-2-vinylcyclopropanes (*1*) with methyllithium.

Materials. Most of the compounds *1* recorded in Table 1 were prepared from the corresponding dienes by addition of dibromocarbene, generated from bromoform and base under conditions of phase transfer catalysis (Method A)[9] or by the Doering-Hoffmann method[10] (Method B). Some of the compounds in Table 1 had previously been prepared by the latter method,[11] but here this method was only used when method A failed due to ring opening and other side reactions. As expected, addition of dibromocarbene to unsymmetrically substituted dienes often resulted in mixtures of two isomeric monoadducts *1* besides bisadducts. In some cases the monoadducts could

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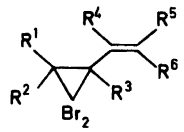
Table 1. Alkenyl-*gem*-dibromocyclopropanes (*1*) from dienes and dibromocarbene.



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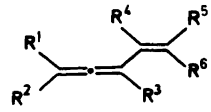

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R^1	R^2	R^3	R^4	R^5	R^6	Compound *1*	Method of preparation	Spectral data
H	H	H	H	H	H	*a*[11]	A	
Me	H	H	H	H	H	*b*	A	IR (film) 980 (s), 920 (s), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (3H, d, *J* 6.4 Hz) 1.5–2.5 (2H, m) 5.1–5.5 (3H, m)
H	Me	H	H	H	H	*c*	A	IR (film) 990 (s), 910 (s), 650 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.1–1.9 (2H, m) 1.35 (3H, br.s.) 4.9–5.8 (3H, m)
H	H	Me	H	H	H	*d*[11]	A	
H	H	H	Me	H	H	*e*	D	IR (film) 1645 (m), 885 (s), 660 (s) cm^{-1} ^1H NMR(CCl_4) δ 1.6–2.2 (3H, m) 1.93 (3H, br.s) 4.67 (1H, br.s) 5.00 (1H, br.s)
H	H	H	H	Me	H	*f*	A	IR (film) 960 (s), 680 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.3–2.5 (3H, m) 1.73 (3H, d, J 6.0 Hz) 5.15 (1H, dd, *J* 7.0 and 15.5 Hz) 5.72 (1H, dq, *J* 6.0 15.5 Hz)
H	H	H	H	H	Me	*g*	A	IR (film) 770 (m) 740 (s) cm^{-1}; ^1H NMR $CDCl_3$) δ 1.2–2.8 (3H, m) 1.77 (3H, dd, *J* 1.5 and 7.0 Hz) 4.8–5.4 (1H, m) 5.5–6.2 (1H, m)
Me	H	H	H	H	Me	*h*	A	IR (film) 740 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.9–2.6 (2H, m) 1.11 (3H, d, *J* 7.6 Hz 1.72 (3H, d, *J* 6.0 Hz) 4.7–5.2 (1H, m) 5.3–6.0 (1H, m)
H	Me	H	H	Me	H	*i*	A	IR (film) 960 (s), 740 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.3–1.9 (2H, m) 1.73 (3H, dd, *J* 1.1 and 6.2 Hz) 4.9–5.3 (1H, m) 5.67 (1H, dq, *J* 6.2 and 15.1 Hz)
H	H	Me	Me	H	H	*j*[11]	A	
Me	Me	H	H	H	H	*k*	B	IR (film) 1630 (m), 1000 (m), 915 (s), 650 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (3H, s) 1.44 (3H, s) 1.7–2.1 (1H, m) 5.2–5.6 (3H, m)
H	H	H	H	Me	Me	*l*	B C	IR (film) 830 (w) 690 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.38 (1H, dd, *J* 7.0 and 7.3 Hz) 1.80 (6H, br.s) 1.9–2.5 (2H, m) 4.90 (1H, br.d. *J* 7.0 Hz)
Me	Me	Me	H	H	H	*m*	C	IR (film) 1630 (m), 990 (m), 920 (m), 800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3H, s) 1.31 (3H, s) 1.38 (3H, s) 5.18 (1H, dd, *J* 1.0 and 7.2 Hz) 5.34 (1H, d, *J* 1.0 Hz) 5.8–6.1 (1H, m)
H	Me	H	H	Me	Me	*n*	D	IR (film) 790 (s), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8–2.9 (2H, m) 1.29 (3H, s) 1.70 (6H, s) 4.80 (1H, br., d, *J* 7.6 Hz)

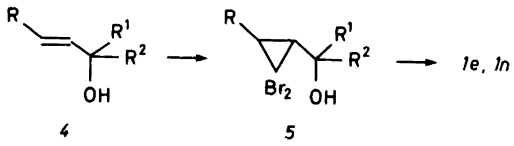
H	H	Me	H	Me	Me	*o*[11]	A C	
Me	Me	H	H	Me	Me	*p*[11]	B	
H	H	H	$-(CH_2)_4-$		H	*q*	A	IR (film) 608 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.9–2.5 (11H, m) 5.3–5.6 (1H, m)
H	$-(CH_2)_4-$		H	H	H	*r*	E	IR (film) 1630 (m), 990 (m), 910 (m), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.3 (9H, m) 5.0–5.3 (2H, m) 5.95 (1H, dd., *J* 10.4 and 16.5 Hz)
Ph	H	H	H	H	H	*s*	E	IR (film) 1640 (w), 920 (m), 780 (m) 730 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5–2.8 (2H, m), 5.2–5.6 (3H, m) 7.1–7.6 (5H, m)
H	Ph	H	H	H	H	*t*	E	IR (film) 1640 (m), 980 (m), 920 (s), 850 (m), 700 (s), 650 (m), cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.4–2.9 (2H, m), 5.1–6.0 (3H, m) 7.19 (5H, br.s.)
H	H	Ph	H	H	H	*u*[15]	A	
H	H	H	Ph	H	H	*v*	E	IR (film) 910 (s), 780 (s), 700 (s) cm^{-1} ^1H NMR ($CDCl_3$) δ 1.90 (1H, dd, *J* 7.7, 8.2 Hz), 2.05 (1H, dd, *J* 7.7, 9.7 Hz) 2.55–2.68 (1H, m), 5.04 (1H, br.s.), 5.77 (1H, br.s), 7.2–7.6 (5H, m).
H	H	H	H	Ph	H	*1w*[16]	A[a]	
H	H	H	H	H	Ph	*1x*	A	IR (film) 790 (m), 760 (m), 695 (s), 680 (m), cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (1H dd, *J* 7,2, 7.6 Hz), 1.99 (1H, dd, *J* 7.2, 10.0 Hz), 2.4–2.7 (1H, m), 5.35 (1H, dd, *J* 8.2, 11.2 Hz) 6.69 (1H, dd, *J* 1.0, 11.2 Hz) 7.1–7.5 (5H, m)

[a] Also prepared by employing $PhHgCBr_3$[41] as the source of dibromocarbene (see Experimental Part).

be separated by distillation or preparative GLC, but in other cases we had to resort to a selective reaction on one of the isomers in order to obtain a separable mixture. This was achieved by treating the mixture with 9-borabicyclo-[3.1.1]nonane (9-BBN) followed by oxidation of the organoborane with alkaline hydrogen peroxide to the corresponding alcohol, which was easily separated from the unreacted isomer by column chromatography on silicagel. The sequence was successfully used in obtaining pure samples of compounds *1l*, *1o* and *1q*. The phenyl-substituted derivatives *1u*, *1w* and *1x* were prepared employing method A. As far as we could determine addition to (*E*)- and (*Z*)-1-phenyl-1,3-butadiene occurred at the terminal double bond only. In both cases reaction times in excess of 48 h at room temperature were required for completion, resulting in yields of only about 30 % due to polymerization. Compound *1x* is configurationally unstable rearranging to the (*E*)-isomer (*1w*) slowly even at −20 °C.

In some cases the desired adducts were not obtained or the yields were very poor by methods A and B, and we had to employ other reactions. Treatment of 2,2-dibromocyclopropanecarbaldehyde[12] and 2,2-dibromo-1,2,3-trimethylcyclopropanecarbaldehyde with isopropylidene- and methylenetriphenylphosphorane, respectively, gave *1l* and *1m* in acceptable yields (Method C). The Wittig reaction failed, however, with several other analogous aldehydes and ketones under a variety of conditions, and it does not appear to be a general method for the preparation of compounds *1*.

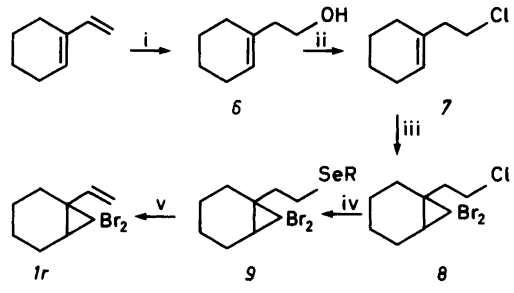
Compound *1c* could not be obtained from the addition of dibromocarbene to isoprene using either method A or B; *1d* was practically the sole product. Moreover, addition to (*E*)-2-methyl-2,4-hexadiene gave a mixture of the expected adducts, but they could not be separated even with the use of the hydroboration-oxidation



Scheme 2. *a*, R=H, $R^1=R^2$=Me. *b*, R=Me, R^1=i-Pr, R^2=H.

method. Hence, compounds *1c* and *1n* were prepared by the sequence of reactions outlined in Scheme 2. Addition of dibromocarbene to the allylic alcohol *4a* by either method A or B gave the alcohol *5a* in poor yield, while a moderate yield of *5b* was obtained from *4b* using the former method. Using *p*-toluenesulfonic acid, dehydration to the olefin was successful in the case of *5a*, and *1e* was obtained in 59 % yield. The same reaction failed with *5b*, but the olefin *1n* was formed besides the expected bromide, when *5b* was treated with carbon tetrabromide and triphenylphosphine.

A mixture of the isomers *1q* and *1r* was obtained from dibromocarbene addition to 1-vinylcyclohexene. The isomers could not be separated by either distillation or preparative GLC. However, using the hydroboration-oxidation method on the mixture, pure *1q* was obtained. On the other hand, the isomer *1r* was successfully prepared by the route depicted in Scheme 3 (Method E). The homoallylic chloride *7* was obtained from the corresponding alcohol *6*,[13] using carbon tetrachloride and triphenylphosphine, and subsequent addition of dibromocarbene gave adduct *8* in high yield. Conversion of this compound to the selenide *9* with sodium chlorophenylselenide in the presence of catalytic amounts of sodium iodide proceeded in high



Scheme 3. R=4-ClC_6H_5-; i, 9-BBN/HOO^-; ii; CCl_4, Ph_3P; iii, $CHBr_3$, NaOH, TEBA (cat.); iv, $(RSe)_2$; v, Chloramine-T.

yield as well, but all the standard* methods for oxidative elimination of selenyl groups gave only very low yield of the desired olefin; however, the use of sodium *N*-chloro-*p*-toluenesulfonamide (chloramine T) under phase transfer conditions[14] furnished *1r* in 64 % yield. The phenyl substituted compounds *1s*, *1t* and *1v* were also prepared by this method. In the latter case, the yield was poor by the normal procedure because chloramine T apparently reacted with the double bond of *1v*. The yield was drastically improved, however, by performing the reaction in the presence of isoprene as co-solvent.

For several of the preparations the overall yields of *1* were poor, but no attempt was made to improve these, since sufficient amounts of the desired compounds were secured.

Reactions with methyllithium. Some of the compounds recorded in Table 1 were quite unstable both thermally and toward oxygen, and freshly prepared samples were used for reactions with methyllithium. With one exception, these were carried out at −78 °C under closely similar conditions; due to low solubility in ether, the reaction of compound *1p* was run at −20 °C with high dilution. It is important that the reactions were carried out at the same temperature because it affects the rates of ring opening and rearrangement differently to a significant extent.[4]

The results are summarized in Table 2. The volatile products from all reactions, except that from the tetrasubstituted derivative *1m*, consisted of either cyclopentadienes, vinylallenes or a mixture of the two. The product ratios are based on GLC analyses which were performed on all reaction mixtures immediately after completion, in order to minimize errors due to dimerization and polymerization. In this way we were able to obtain quite reproduceable ratios of cyclopentadiene to allene. In some cases, however, the low thermal stability of the products required that the mixture was hydrogenated catalytically prior to analysis by GLC. The yields in these reactions as determined by GLC, using internal standard, were practically quantitative.

With the exception of 5,5-disubstituted derivatives, cyclopentadienes undergo thermally induced 1,5-H shifts. Monosubstituted derivatives undergo the isomerization at a significant rate even at 0 °C. However, in all cases the structures of the initially formed isomers could be established by trapping them as the [4+2] cycloadducts

Table 2. Products from reactions of *1* with methyllithium at −78 °C.

Entry	Substrate (*1*)	Products (%)[a] 1,3-cyclopentadiene	Allenes[b]
1	*a*	1,3-Cyclopentadiene (*10*); (89)	*2a*[21,22] (11)
2	*b*	–	*2b*[23] (100)
3	*c*	2-Methyl-(*11*); (68)	*2b* (32)
4	*d*	*11*, 1-methyl-(*12*); (99)[c]	*2d*[21,22] (1)
5	*e*	*11*, *12*; (96)[c]	*2e*[24] (4)
6	*f*	*11*; (87)	*2f*[21,22] (13)
7	*g*	–	*2g*[21,22] (100)
8	*h*	–	*2h* (100)
9	*i*	2,5-Dimethyl-(*13*)[17]; (68)	*2i*[2] (32)
10	*j*	1,2-Dimethyl-(*14*)[17]; (99)	*2j*[2] (1)
11	*k*	–	*2k*[23] (100)
12	*l*	–	*2l*[25] (100)
13	*m*	Complex mixture[d]	
14	*n*	–	*2n* (100)
15	*o*	2,5,5-Trimethyl-(*15*)[2]; (85)	*2o* (15)
16	*p*	–	*2p*[26] (100)
17	*q*	*16*, *17* (83) (17)	
18	*r*	Same as for *1q*	
19	*s*	–	*2s*[27] (100)
20	*t*	–	*2t* (100)
21	*u*	1-Phenyl-(*19*)[28]; (93)	*2u* (7)
22	*v*	*19* (78)	*2v* (22)
23	*w*	2-Phenyl-(*20*)[28]; (71)	*2w*[29] (29)
24	*x*	–	*2x* (100)

[a] Based on an average of two runs not differing more than 2 %. [b] See Scheme for notation. [c] A 53:47 mixture of *11* and *12*, respectively. [d] Several isomeric bicyclo [1.1.0] butanes were formed, besides other products.

with *N*-phenylmaleimide at −78 °C. The structures of the adducts were determined spectroscopically and by comparison with authentic samples as well. All the cyclopentadienes had been described previously in the literature, although not always in a pure state.

The cyclopentadiene formed from the reaction of *1i* (entry 9) was shown to be 2,5-dimethyl-1,3-cyclopentadiene (*13*); 1,5-H shifts are known to produce the thermodynamically more stable 1,3- and 1,4-dimethyl isomers[17] but these were not detected in the product mixture. The reaction of *13* with *N*- phenylmaleimide gave a 2:1 mixture of isomeric adducts, differing structurally only in the configuration of the methyl group at the bridgehead carbon. In the ^{1}H NMR spectrum of the major component, the olefinic proton appears at δ 5.60, shifted 0.17 ppm upfield from that of the minor component. A comparison with spectra of similar *N*-phenylmaleimide adducts reveals that a bridgehead methyl *syn* to the double bond exerts a deshielding effect on the olefinic proton; in the adduct from *15*, which is substituted with a *gem.* dimethyl group at the bridgehead, the olefinic proton appears at δ 5.72, while with a methylene bridgehead as in the adduct from *14* this proton resonates at δ 5.53. We therefore conclude that the major component is the *anti* isomer. The products from *1q* and *1r* (entries 17 and 18) were identical according to GLC. Reaction of either with *N*-phenylmaleimide gave the same 5:1 mixture of adducts derived from the isomeric bicyclo[4.3.0]-nonadienes *16* and *17*, respectively. Attempts on isolation of compound *17* resulted in partial conversion to the thermodynamically most stable isomer 18[18] and some unidentified products.

The cyclopentadiene fractions from reactions of the dibromides *1u*, *1v* and *1w* (entries 21, 22 and 23) consisted of mixtures of 1- and 2-phenylcyclopentadienes as indicated by the presence of resonances due to the allylic protons at δ 3.23 and 3.50, respectively; the 1-isomer (*19*) dominated in the products from *1u* and *1v*, while the 2-isomer (*20*) in that from *1w*. However, the adducts with *N*-phenylmaleimide formed from the crude reaction mixtures revealed that the minor isomers in each case actually arose from 1,5-H shifts during isolation.

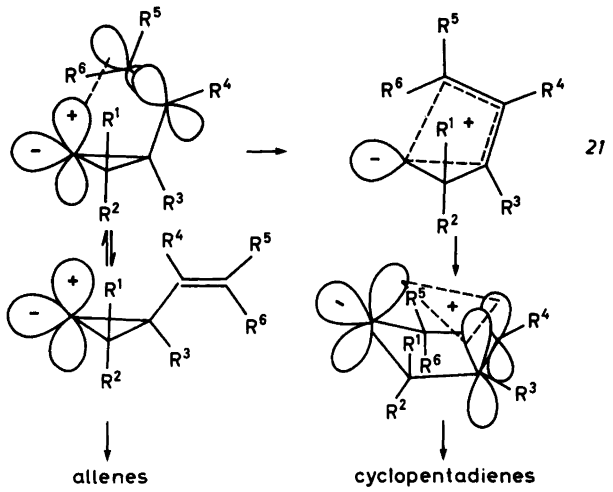
Conjugated vinylallenes are reactive substances[19] which are not always readily purified. The allenes *2g*, *2h*, *2l*, *2n*, *2o* and *2p* are prone to undergo thermal 1,5-H shifts with formation of the corresponding conjugated trienes. Preparative GLC was therefore not always applicable, but samples pure enough for spectroscopic identification were obtained for most of the allenes in Table 2, using other standard chromatographic techniques as well. Moreover, in some cases the hydrogenation products were identified by comparison with authentic samples.

The reaction of *1m* with methyllithium afforded a complex mixture of products including bicyclo[1.1.0]butane derivatives. Clearly, 1,3-insertion of the cyclopropylidene into a C−H bond is a competitive reaction which has been observed previously for a number of other tetrasubstituted dibromocyclopropanes.[20] The characterization of the products from *1m* will be the subject of a separate communication.

DISCUSSION

The results of Table 2 clearly show that the methyl group exerts a pronounced effect on the ratio of cyclopentadienes to allenes in the products. This is perhaps not surprising, since experiments by Brinker and Ritzer[4] and MINDO/3 calculations by Schoeller and Brinker[6] indicate that the activation energies for the ring opening to vinylallene and the carbene rearrangement leading to cyclopentadienes are comparable in size. Hence, small changes in the nature of the substituents could lead to significant changes in product composition. Obviously, substituents can effect the rates of both ring opening and carbene rearrangement, and the observed effect is a combination of electronic and steric interactions. Only a few studies have been published regarding substituent effects on the ring opening.[30] It appears that this reaction is not strongly influenced by electronic effects, but the fact that tetraalkyl-substituted cyclopropylidenes prefer C−H insertion to ring opening[20] is indicative of a steric effect retarding the latter. As a first approximation, however, it seems reasonable to propose that methyl and phenyl groups exert their effect mainly on the carbene rearrangement and essentially as a steric interaction.

A possible reaction path for the carbene-carbene rearrangement is depicted in Scheme 4. For simplicity free carbenes are represented, but complexation with lithium bromide and solvation

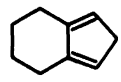


Scheme 4.

are most probable. A bicyclopentane-like transition state (*21*) is reached through an overlap between the empty p-orbital of the carbenyl carbon and the π-orbital of the double bond. Any hindrance to this essential interaction will decrease the rate of rearrangement. According to this simplified representation, molecular models reveal the following steric substituent effects: i) a terminal group on the double bond *cis* to the three-membered ring (R^6) should disfavour rearrangement, while the corresponding *trans* substituent (R^5) should have no effect; ii) only the substituent on the three-membered ring that is *cis* related to the double bond (R^1) should retard the rate of rearrangement, and iii) substituents at the carbon atoms connecting the ring and double bond (R^3 and R^4) should have little effect.

Referring to the results recorded in Table 2, the ratio of 8:1 for cyclopentadiene (*10*) to 1,2,4-pentatriene (*2a*), obtained from reaction of the unsubstituted *1a* (entry 1), is regarded as the normal value; deviations from this number reflect a substituent effect. With one exception (entry 15), all reactions of the compounds with *cis* substituents arranged according to i) gave allenes as sole products (entries 7,8,12,14 and 24), and rearrangement was the main reaction path for those with *trans* substituents (entries 6,9 and 22). As expected, the reaction of *1p* (entry 16) gave the allene *2p* exclusively, but it should be noted that in this case rearrangement would lead to a tetramethylcyclopentenylidene which cannot form a cyclopentadiene by 1,2-hydrogen shift. The predictions of ii) are also generally born out by the experiments. Allenes are sole products from compounds with *cis* substituents (entries 2,8,11 and 19), while with *trans* substituents cyclopentadienes are major products in two cases (entries 3 and 9), although the ratios to allenes are reduced compared with the normal value. On the other hand, no cyclopentadiene was formed from the reaction of *1t* (entry 20). With substituents according to iii) cyclopentadienes are main products and the ratios are actually increased (entries 4,5,10 and 21).

The general trend of the content of Table 2 is in accordance with the above proposition that steric substituent effects govern the rate of carbene rearrangement in reactions of compounds *1* with methyllithium. Recent work by Brinker and co-workers also supports this notion.[8,31] However, the results from two reactions (entries 15 and 20) appeared contradictory. In spite of a *cis* arranged methyl group, compound *10* produced mainly the cyclopentadiene *15*, while the similar compounds *1l* and *1n* gave the corresponding allenes as sole products (entries 12 and 14). The main structural difference between the three compounds is the presence of a methyl group in *1o* at the ring carbon carrying the double bond. For compounds *1l* and *1n* the preferred conformations have the double bond twisted away from the carbenyl carbon, rendering the essential $p-\pi$ orbital overlap unlikely. A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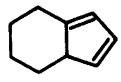
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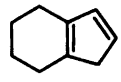
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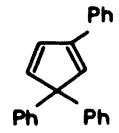

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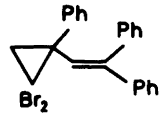

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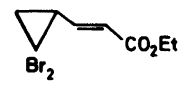

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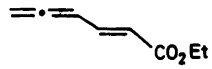

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similar twist is not possible in the case of *1o* without causing considerable steric interference between the methyl groups on the ring and double bond. We assume that this conformation is energetically less favourable than that required for the $p-\pi$ overlap and thereby providing an explanation for the apparent abnormal behaviour of *1o*. A similar result has recently been reported by Zimmerman and Kreil;[32] 2,5,5,-triphenyl-1,3-cyclopentadiene (*22*) is the initial product formed in the reaction of the dibromocyclopropane derivative *23* and butyllithium.

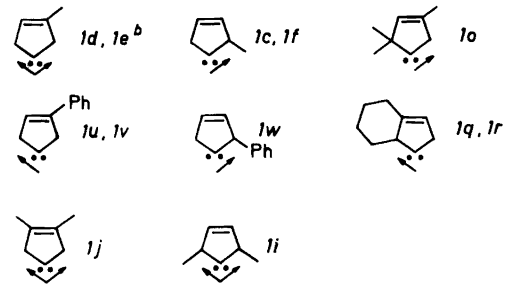
The reaction of *1t* afforded the allene *25* exclusively. Since no steric interaction that should retard the rearrangement is obvious in *1t*, the corresponding cyclopentadiene was the anticipated main product. Hence it appears that compounds with R^2=phenyl and to a lesser extent R^2=methyl enhance the rate of ring opening by an electronic effect. The data of Table 2 further suggest that R^4=methyl enhances electronically the rate of carbene rearrangement, while *trans* substituents on the double bond (R^5=Me, Ph) cause only minor changes to the product ratio. Further work is necessary in order to ascertain these electronic effects and also to establish the influence of strongly electron attracting and donating groups on the reactions. Calculations[6] predict that the carbene rearrangement is disfavoured by electronegative substituents on the double bond, and preliminary results from our laboratory show that the ester *24* reacts with methyllithium to afford the corresponding allene *25* as sole product.

The bicyclic compounds *1q* and *1r* form special cases. Both react with methyllithium to give the same mixture of bicyclic compounds *16* and *17* in accordance with the rearrangement mechanism which requires the same cyclopentenylidene to be formed from either starting material. It was unexpected that *16* and *17* were sole products, particularly from the reaction of *1r*, since reaction of the related compound 7,7-dibromobicyclo[4.1.0]heptane with methyllithium afforded tricyclic compounds[33] as products of intramolecular insertion. The formation of bicyclobutanes from the reaction of *1m* demonstrates that intramolecular C–H insertion may become competitive with the carbene rearrangement.

The results also reveal that the presumed 3-cyclopentenylidenes prefer 1,2-insertion into tertiary rather than secondary C–H bonds. This is actually consistent with results previously obtained for other carbenes.[3] The selective formation of cyclopentadiene *19* from *1u* and *1v*, however, is probably due to a conjugative effect. The various modes of insertion are depicted in Table 3.

The present study indicates that it is possible, on essentially steric grounds, to predict with a useful degree of certainty the product composition from reactions of alkyl and phenyl substituted *gem*-dibromocyclopropanes of the general structure *1* with methyllithium. Conversely, the results give support to a mechanism for the rearrangement as outlined in Scheme 4.

Table 3. 1,2-H migration in 3-cyclopentenylidenes derived from compounds *1*.[a]



[a] Arrows indicate the direction of double bond formation. Two linked arrows mean exactly or close to 1:1; one arrow means dominating (>2/3) or in only one direction. [b] The corresponding *gem*-dibromovinylcyclopropane (see Table 1).

EXPERIMENTAL

NMR spectra were recorded on Varian EM 360A, JEOL JNM FX60 and JEOL FX 90Q spectrometers. Elemental analyses were performed by I. Beetz Microanalytical Laboratory, 8640 Kronach, West Germany. Satisfactory analyses were obtained for all compounds submitted.

General procedures for preparation of gem-*dibromocyclopropanes* 1. Method A. Reactions were carried out by the phase transfer technique essentially as described in the literature,[9] using a diene, bromoform, 50 % aq. NaOH and cat. amounts of benzyltriethylammonium chloride (TEBA) at ambient temperature.

Method B. Reactions were carried out as described in the literature,[10,11] from diene, bromoform and potassium *t*-butoxide at ~−10 °C.

Separation of isomers by hydroboration/oxidation. A solution of 1.5 eq. of 9-BBN (0.5 M in THF) was added with stirring to a solution of the isomer mixture in THF at room temperature. Stirring continued until only one isomer was left (GLC, 10 % SE 30). The organoboranes were oxidized with H_2O_2/NaOH in the usual way for 1 h at 40 °C before addition of water and extraction with ether. Unreacted olefin was obtained by column chromatography (SiO_2/hexane) followed by distillation.

cis-*1,1-Dibromo-3-methyl-2-vinylcyclopropane* (*1b*) and *1,1-dibromo-2-(Z-propenyl)cyclopropane 1g)* were formed as a 1:1.3 mixture in 60 % yield, b.p. 57−58 °C (4.5 mmHg). The isomers were separated by prep. GLC (20 % SE 30, 100 °C), *1b* having the shortest retention time.

trans-*1,1-Dibromo-3-methyl-2-vinylcyclopropane* (*1c*) and *1,1-dibromo-2-(E-propenyl)cyclopropane (1f)* were formed as a 1:2 mixture in 81 % yield. They were separated by fractionation on a "Fischer Spaltrohr" column: *1c*, b.p. 57 °C (8 mmHg) and *1f*, b.p. 67 °C (10 mmHg).

trans-*1,1-Dibromo-3-methyl-2-[(E)-propenyl]-cyclopropane (1i)*, was obtained in 70 % yield, b.p. 60−62 °C (2.5 mmHg).

2,2-Dibromo-1,3,3-trimethylcyclopropanecarbaldehyde (3b). A solution of 1.36 g (5.0 mmol) of 2,2-dibromo-1,3,3-trimethylcyclopropylmethanol[34] and 3.0 g (8.0 mmol) of pyridinium dichromate in 20 ml of CH_2Cl_2 was stirred at room temp. until all the alcohol had been consumed (30 h). The reaction mixture was diluted with ether, filtered and worked up in the usual way to give 1.11 g (87 %) of *3b*,[35] m.p. 64 °C.

1,1-Dibromo-2,3,3-trimethyl-2-vinylcyclopropane (1m). A 0.52 M solution of methylenetriphenylphosphorane in THF/hexane was added dropwise to a stirred solution of 4.05 g (15 mmol) of aldehyde *3b* in 50 ml of THF, kept at −40 °C, until the yellow colour persisted. HMPA (3,5 ml, 20 mmol) was added all at once, and the solution was allowed to reach room temperature overnight. The reaction was terminated by adding 50 ml of water and the product isolated in the usual way. Triphenylphosphine oxide was precipitated by addition of some hexane. Distillation gave 3.55 g (88 %) of the olefin *1m*, b.p. 63−65 °C (0.8 mmHg). The compound solidified upon cooling (0 °C) and a sample was recrystallized from methanol, m.p. 23−24 °C.

2-(2,2-Dibromocyclopropyl)propan-2-ol (5a) was prepared in 2 % yield from 2-methyl-3-buten-2-ol (*4a*) $CHBr_3$ and aqueous NaOH under conditions of phase transfer catalysis,[9] b.p. 43−44 °C (2 mmHg). IR (film) 3580 (s), 3460 (s), 680 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (3H, s) 1.55 (3H, s) 1.6−1.9 (3H, m) 2.0 (1H, br. s).

1,1-Dibromo-2-isopropenylcyclopropane (1e). The alcohol *5a* (0.39 g, 1.5 mmol) and 26 mg (0.15 mmol) of p-toluenesulfonic acid was heated at 150 °C for 30 min. Distillation, followed by column chromatography (SiO_2-hexane) gave 0.21 g (59 %) of *1e*, b.p. 58−60 °C (8 mmHg).

*1-(*trans-*2,2-Dibromo-3-methylcyclopropyl)-2-methyl-1-propanol (5b)* was prepared in 37 % yield from (*E*)-2-methyl-4-hexen-2-ol[36] (*4b*), bromoform and aq. NaOH under normal conditions of phase transfer catalysis,[9] b.p. 58−60 °C (0.01 mmHg), m.p. 26−27 °C. IR (film) 3470 (m), 1040 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (3 H, d *J* 6.8 Hz) 1.03 (3H, d. *J* 6.8 Hz) 1.1−1.5 (2H, m) 1.31 (3H, s) 1.83 (1H, m) 2.34 (1H, s) 3.11 (1H, dd *J* 6.5 and 8.9 Hz).

trans-*1,1-Dibromo-3-methyl-2-(2-methyl-1-propenyl)cyclopropane (1n).* A solution of 5.25 g (20 mmol) of triphenylphosphine, 2.57 g (9 mmol) of *5b* and 6.64 g (20 mmol) of CBr_4 was stirred at room temperature until all of *5b* had been consumed (22 h). The reaction mixture was worked up in the usual way. After several distillations 0.37 g (12 %) of pure *1n* was obtained, b.p. 56−57 °C (1.5 mmHg). A second product was the tribromide which was not obtained pure.

1,1-Dibromo-2-methyl-2-(2-methyl-1-propenyl)cyclopropane (1o), b.p. 56−57 °C (1.3 mmHg), was obtained pure after the isomer 1,1-dibromo-3,3-dimethyl-2-(2-propenyl)cyclopropane was converted selectively to the corresponding alcohol by the hydroboration method.

1,1-Dibromo-3,3-dimethyl-2-vinylcyclopropane (1k) and *1,1-dibromo-2-(2-methyl-1-propenyl)cyclopropane (1l)* were formed as a 2.5:1 mixture in 53 % yield. Fractionation on a 1 m

spinning band column gave pure *1k*, b.p. 43–46 °C (0.4 mmHg). In the residue *1k* was converted to the corresponding alcohol by the hydroboration-oxidation procedure, enabling the isolation of pure *1l*. The latter was obtained in 54 % yield from a reaction of 2,2-dibromocyclopropanecarbaldehyde[12] (*3a*) with an ether solution of isopropylidenetriphenylphosphorane in the usual way.

1,1-Dibromo-3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropane (1p) was prepared according to method B in 41 % yield, m.p. 38–39 °C (lit.[11] m.p. 40–41 °C). The improvement in yield compared with that of the lit.[11] was achieved using a 50 % excess of diene, reaction temp. at −20 °C and quenching with phosphate buffer (pH 6); the temperature during isolation never exceeded 25 °C. The product was recrystallized several times from pentane at −20 °C.

1,1-Dibromo-2-(1-cyclohexenyl)cyclopropane (1q) was formed in 64 % yield as a 2:3 mixture with the isomer *1r*. Applying the hydroboration-oxidation procedure pure *1q* was obtained, b.p. 56–58 °C (0.001 mmHg).

1-(2-Chloroethyl)-1-cyclohexene (7). The hydroboration of 1-vinylcyclohexene with diisoamylborane followed by oxidation gave 2-(1-cyclohexenyl)ethanol[13] (*6*) in 56 % yield. The alcohol was treated with triphenylphosphine and CCl_4 in the usual way furnishing the chloride *7* in 81 % yield, b.p. 83–85 °C (18 mmHg); IR (film) 910 (s), 730 (s), 650 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3–1.7 (4H,m) 1.7–2.1 (4H, m) 2.32 (2H, t, *J* 7.3 Hz) 3.49 (2H, t, *J* 7.3 Hz) 5.42 (1H, br.s).

1-(2-Chloroethyl)-7,7-dibromobicyclo[4.1.0]-heptane (8) was prepared in 95 % yield from *7* and dibromocarbene, generated by method A. IR (film), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.4 (9H, m) 2.10 (2H, t, *J* 7.7 Hz) 3.67 (2H, dt, *J* 2.0 and 7.7 Hz).

7,7-Dibromo-1-vinylbicyclo[4.1.0]heptane (1r). A mixture of 0.95 g (3.0 mmol) of *8*, 0,95 g (4.6 mmol) of sodium *p*-chlorophenylselenide and 80 mg (0.5 mmol) of NaI in 30 ml of ethanol was heated with reflux until all the chloride had reacted (24 h). The selenide formed was admixed with 2.5 molar equivalents of chloramine T, 40 mg TEBA, 20 ml of benzene and 20 ml of 0.5 M phosphate buffer (pH 8) and vigourously stirred at room temperature until all the selenide had reacted (20–30 h). After work-up and column chromatography of the crude product, *1r* was obtained in 64 % yield.

(Z)-4-Chloro-1-phenyl-1-butene (26). The alcohol (*Z*)-4-phenyl-3-buten-1-ol[38] was prepared from 1-phenyl-1,3-butadiene[39] in 59 % yield by the hydroboration method using isoamylborane. The crude product, 6.5 g, (50 mmol), and 15.7 g (60 mmol) of triphenylphosphine in 50 ml of CCl_4 were heated under reflux for 2 h and worked up in the usual way. Distillation gave 5.3 g (64 % yield from the diene) of *26* b.p. 72–73 °C (2.5 mmHg). IR (film) 770 m, 700 (s) cm^{-1}; ^1H NMR (CCl_4): δ 2.5–2.9 (2H, m) 3.41 (2H, t, *J* 7.0 Hz) 5.3–5.7 (1H, m) 6.39 (1H, br. d, *J* 11.8 Hz) 7.08 (5H, br.s).

cis-*1,1-Dibromo-3-(2-chloroethyl)-2-phenylcyclopropane (27)* was prepared from *26* and dibromocarbene according to method A in 39 % yield. IR (film) 740 (s), 700 (s). ^1H NMR ($CDCl_3$): δ 1.4–2.4 (3H, m) 3.00 (1H, d, *J* 11.0 Hz) 3.70 (2H, t, *J* 6.5 Hz) 7.0–7.4 (5H, m).

cis-*1,1-Dibromo-2-phenyl-3-vinylcyclopropane (1s)*. Compound *27* was converted to the selenide and treated with chloramine T under phase transfer conditions as described for *1r*. The overall yield of *1s* was 42 %.

trans-*1,1-Dibromo-3-(2-chloroethyl)-2-phenylcyclopropane (28)* was prepared from (*E*)-4-chloro-1-phenyl-1-butene,[37] according to method A in 49 % yield; IR (film) 750 (m), 730 (m), 690 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.9–2.5 (3H, m) 2.59 (1H, d, *J*, 7.6 Hz) 3.76 (2H, t, *J* 6.0 Hz) 7.2–7.5 (5H, m).

trans-*1,1-Dibromo-2-phenyl-3-vinylcyclopropane (1t)*. Compound *28* was converted to the selenide and treated with chloramine T under phase transfer conditions as described for *1r*. The overall yield of *1t* was 42 %.

4-Chloro-3-phenyl-1-butene (29); was prepared in 72 % yield from 2-phenyl-3-buten-1-ol,[40] CCl_4 and triphenylphosphine as described for *26*, b.p. 83–84 °C (1.5 mmHg). IR (film) 990 (s), 920 (s), 700 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.6–3.7 (3H, m) 5.0–5.2 (2H, m) 5.9–6.1 (1H, m) 7.1–7.3 (5H, m).

1,1-Dibromo-2-(2-chloro-1-phenylethyl) cyclopropane (30). A stirred mixture of 2.50 g (15 mmol) of the chloride *29* and 13.24 g (25 mmol) of phenyl(tribromomethyl)mercury[41] in 100 ml of dry benzene was heated under reflux for 7 h. After work-up in the usual way, 1.49 g (29 %) of *30* was obtained as a mixture of diastereomers. ^1H NMR ($CDCl_3$) 1.2–2.2 (3H, m) 2.7–3.0 (1H, m) 3.81 and 3.96 (2H, two d; J. 6.0,6.3) 7.2–7.4 (5H, m).

1,1-Dibromo-2-(1-phenylethenyl)cyclopropane (1v). Compound *30* was converted to the selenide as described for *1r*. A mixture of 395 mg (0.8 mmol) of the selenide, 282 mg (1.0 mmol) of chloramine T, 40 mg (20 mmol) of TEBA in 4 ml of isoprene, 12 ml of $CHCl_3$ and 16 ml of 1*M* phosphate buffer (pH 8) was stirred vigorously at room temperature for 9 h. Workup gave 161 mg (67 %) of *1v*.

1,1-Dibromo-2-[(E)-2-phenyl-1-ethenyl]cyclopropane (*1w*) was prepared in 59 % yield from (*E*)-1-phenyl-1,3-butadiene and phenyl(tribromomethyl)mercury in the usual way.[41] Using method A_1 a yield of 40 % is reported in the literature.[16]

1,1-Dibromo-2-[(Z)-2-phenyl-1-ethenyl]cyclopropane (*1x*). The reaction between dibromocarbene and (*Z*)-1-phenyl-1,3-butadiene was very slow by method A. The reaction mixture was stirred for a total of three days while extra bromoform (0.2 and 0.1 equivalents) was added after 24 and 48 h., respectively. The hydroboration/oxidation procedure was applied to remove some unreacted diene, giving *1x* in 31 % yield. The compound isomerized slowly to the *E*-isomer on standing, even at −20 °C.

General procedure for the reaction of gem-dibromocyclopropanes with MeLi. An etheral solution of 1.6 M MeLi (1.0 ml) was added within 5 min to a stirred solution of 1.0 mmol of *gem*-dibromovinylcyclopropane derivative *1* in 2 ml of dry ether at −78 °C. After stirring for 1 h at this temperature, 1 ml of water was added and the organic fraction analysed. The yields were generally in the range 90−100 % as determined by GLC using internal standard. A larger scale was used when the products were isolated by prep. GLC or distillation.

Hydrogenation procedure. The reaction mixture from *1* and methyllithium was washed with brine at 0 °C until the aqueous phase remained neutral. Ethanol (5 ml) was added, and the mixture hydrogenated for 24 h at 1 atm. using 0.02 g 10 % Pd/C as catalyst.

Adducts of cyclopentadienes. The reaction mixture obtained from 2.0 mmol of the *gem*-dibromocyclopropane *1* and methyllithium was treated with solid CO_2 at −78 °C in order to remove unreacted lithium reagent. At the same temperature a solution of 0.68 g (4.0 mmol) of *N*-phenylmaleimide in 4 ml THF was added all at once, and the reaction mixture left stirring at −78 °C for 12 h before allowed to reach room temperature. Pure adducts were obtained by column chromatography (SiO_2) and recrystallization.

(Z)-2,3,5-Heptatriene (*2h*) was purified by prep. GLC (10 % SE 30, 40 °C); IR (film) 1955 (m), 1945 (m), 1640 (w), 690 (m) cm^{-1}. ^1H NMR ($CDCl_3$); δ 1.6−1.8 (6H, m), 5.6−6.2 (2H, m).

2,5-Dimethyl-1,3-cyclopentadiene (*17*)[14] was identified by reaction with *N*-phenylmaleimide. Two isomeric adducts were formed in a ratio of 2:1. The major one was obtained pure, m.p. 112 °C, from heptane. IR (KBr) 1705 (s), 1380 (m), 1180 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.90 (3H, d, *J* 6.4 Hz), 1.80 (3H, d, *J* 1.4 Hz), 2.13 (1H, br. q, *J* 6.4 Hz) 2.8−3.3 (2H, m), 3.3−3.5 (2H, m), 5.60 (1H, br. s) 6.9−7.5 (5H, m). The minor isomer had a very similar ^1H NMR spectrum; the doublet at δ 0.90 was shifted to 0.83 and the singlet at 5.60 appeared at 5.77, while the other resonances were indistinguishable.

6-Methyl-2,3,5-heptatriene (*2n*) was obtained by prep. GLC. IR (film) 1945 (w), 910 (m), 790 (m), 740 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.6−1.8 (9H, m), 4.9−5.3 (1H, m), 5.4−5.7 (1H, m), 5.7−6.1 (1H, m).

Bicyclo[4.3.0]nona-6,9(1)-diene (*16*) and *bicyclo[4.3.0]nona-6,8-diene* (*17*). According to GLC (3 % OV17) near identical product mixtures were obtained from reactions of *1q* and *1r* with methyllithium. The product reacted completely with maleic anhydride. Reaction with *N*-phenylmaleimide gave the adducts from *16* and *17* in a 5:1 ratio. Only the major adduct was obtained pure, m.p. 136 °C (from heptane). IR (KBr) 1770 (m), 1700 (s), 1380 (s), 1190 (s), 730 (s), 690 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.1−1.9 (6H, m), 1.9−2.3 (4H, m), 3.2−3.5 (4H, m), 7.1−7.6 (5H, m). During work-up both *16* and *17* isomerized to bicyclo[4.3.0]nona-1(6),7-diene (*18*) among other products.[18]

1-Phenyl- (19) and *2-phenyl-1,3-cyclopentadiene* (*20*); *3-phenyl-1,2,4,pentatriene* (*2n*). The phenylcyclopentadiene fraction of the product from *1u* and methyllithium was trapped by treating the cold reaction mixture with *N*-phenylmaleimide. The mixture of adducts consisted mainly (>90 %) of that from 1-phenyl-1,3-cyclopentadiene (*19*), m.p. 170 °C (from hexane−benzene 2:1). IR (KBr) 1705 (s), 1380 (m), 1180 (m), 740 (m), 690 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 2.0−2.1 (2H, m) 3.5−3.7 (3H, m) 6.3−6.5 (2H, m), 7.1−7.7 (10H, m). During isolation the isomer *19* isomerized partly to 2-phenylcyclopentadiene (*20*), yielding a 7:3 mixture of the two isomers. The allene 3-phenyl-1,2,4-pentatriene (*2n*) was quite unstable and was not obtained pure. IR (film) 1940 (w), 990 (m), 920 (s) cm^{-1}. Catalytic hydrogenation of the reaction mixture gave cyclopentylbenzene[42] and 3-phenylpentane,[43] characterized by comparison with authentic samples.

4-phenyl-1,2,4-pentatriene (*2v*) was not obtained quite pure by preparative GLC. It was rapidly oxidized in air. The IR spectrum exhibited a sharp band at 1950 cm^{-1}, but a satisfactory ^1H NMR spectrum was not obtained. However, catalytic hydrogenation of the reaction mixture gave cyclopentylbenzene and *sec*-pentylbenzene,[43] characterized by comparison with authentic samples.

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