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CHEMISTRY OF *GEM*-DIHALOCYCLOPROPANES—VI[1]

A NOVEL SYNTHESIS OF CYCLOPENTADIENES AND FULVENES

L. SKATTEBØL
Union Carbide Research Institute P.O. Box 278, Tarrytown, N.Y.

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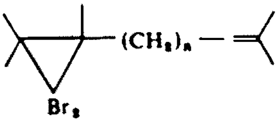
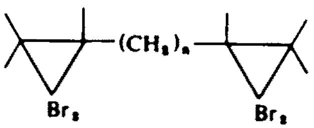
Abstract—Reactions of 1,1-dibromo-2-vinylcyclopropane derivatives with MeLi yielded cyclopentadienes as the main products together with small amounts of allenic compounds (Table 1). By the same reaction 2,2,2′,2′-tetrabromobicyclopropyl derivatives yielded, in all but one case, only small amounts of diallenes; the exception is the exclusive formation of 2,7-dimethyl-2,3,5,6-octatetraene, (XIII) from 2,2,2′,2′-tetrabromo-3,3,3′,3′-tetramethylbicyclopropyl (XII). From two other reactions the major products were identified as 2,6-dimethylfulvene (XVI) and 1,2-dimethylfulvene (XVIII) respectively. Possible mechanisms for the rearrangement leading to the cyclic compounds are discussed.

IN A previous paper[1] the reaction of *gem*-dibromocyclopropanes of the general structures I and II, n > 0, with methyllithium was reported. From compounds where n = 2, tricyclo[4.1.0.0^{4,6}]heptane derivatives were obtained besides the expected allenic compounds, which in the other cases were the major or exclusive products. The present work describes reactions with methyllithium of compounds I and II when these are derivatives of vinylcyclopropane and bicyclopropyl, respectively (n = 0).[2] In most reactions only small amounts of allenes were formed; surprisingly, cyclopentadienes or fulvenes constituted the main part of the products.



I



II

The starting materials were prepared by addition of dibromocarbene to the respective conjugated diene.[3] The reactions with ethereal methyllithium were normally carried out at −78° as previously described.[1,4] Gas chromatographic analysis was always carried out on the ether solution of the product prior to evaporation of solvent. When feasible, pure samples of each compound were obtained by preparative scale gas chromatography. The results from the reactions of the vinylcyclopropane derivatives are summarized in Table 1.

The allenic compounds were quite readily identified despite the small amounts available and their general instability. The sharp intense infrared band in the 1950-

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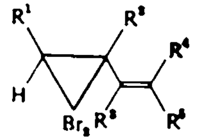
[1] Part V, L. Skattebøl, *J. Org. Chem.* **31**, 2789 (1966).

[2] Part of this study has been reported in a preliminary communication, L. Skattebøl, *Chem. & Ind.* 2146 (1962).

[3] L. Skattebøl, *J. Org. Chem.* **29**, 2951 (1964).

[4] L. Skattebøl, *Acta. Chem. Scand.* **17**, 1683 (1963).

TABLE 1. REACTION OF 2-(1-alkenyl)-1,1-DIBROMOCYCLOPROPANES WITH METHYLLITHIUM AT −78°

		Products (% of mixture)			
		Cyclopentadienes		Allenes	
$R^{1-5} = H$	(III)	Cyclopentadiene	(86)	1,2,4-pentatriene	(14)
$R^2 = Me$	(IV)	1-methyl-	(48)	3-methyl-1,2,4-pentatriene	(17)
$R^1 = R^{3-5} = H$		2-methyl-	(35)		
	(V)[a]	1-methyl-	(14)	1,3,4-hexatriene	(15)
		2-methyl-	(71)	1,2,4-hexatriene	
$R^2 = R^3 = Me$	(VI)	1,2-dimethyl-	(98)	3,4-dimethyl-1,2,4-pentatriene[b]	
$R^1 = R^4 = R^5 = H$					
$R^1 = R^5 = Me$	(VII)	1,3-dimethyl	(48)	*trans*-2,3,5-heptatriene	(32)
$R^2 = R^3 = R^4 = H$		1,4-dimethyl	(20)		
$R^3 = R^4 = R^5 = Me$	(VIII)[c]	2,5,5-trimethyl	(70)	2,5-dimethyl-1,3,4-hexatriene	(7)[d]
$R^1 = R^2 = H$					

[a] Mixture of 1,1-dibromo-2-methyl-3-vinylcyclopropane (40%) and 1,1-dibromo-2-(2-propenyl) cyclopropane (60%).

[b] Not isolated.

[c] Some (<10%) of the isomer 1,1-dibromo-2,2-dimethyl-3-isopropenylcyclopropane was present.

[d] 2,4-Dimethyl-1,3,5-hexatriene was also isolated from this mixture.

cm^{-1} region, characteristic of the allenic grouping, was present in all the samples. The ultraviolet spectra were as expected quite similar to those of related conjugated dienes. A few vinyl allenes have recently been reported.[5,6]

The cyclopentadienes were characterized by both physical and chemical means. The isomer ratio was determined by gas chromatographic analysis on dimethylsulfolane and β,β'-oxydipropionitrile columns. The NMR spectra of the hydrocarbons and their N-phenylmaleimide or maleic anhydride adducts established unequivocally the structures recorded in the Table.[7]

Among the cyclopentadienes recorded in the Table only the 2,5,5,-trimethyl derivative could be distilled practically unchanged, which is in accord with previous observations[10] that the rate of dimerization decreases as the number of methyl substituents increases. Isomerization of 5,5-disubstituted derivatives requires relatively high temperatures.[11] The mixture of 1,3- and 1,4-dimethyl cyclopentadienes did not

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[5] A. A. Petrov and A. V. Fedorova, *Russian Chem. Rev.* **30**, 1 (1964).

[6] [a] M. Bertrand, *C.R. Acad. Sci. Paris* **274**, 824 (1958); [b] R. Srinivasan, *J. Amer. Chem. Soc.* **83**, 2806 (1961); [c] H. Prinzbach and E. Druckrey, *Tetrahedron Letters* 2959 (1965); [d] K. J. Crowley, *Proc. Chem. Soc.* 17 (1964); [e] K. L. Mikolajczak, M. O. Bagley, R. B. Bates and I. A. Wolff, *J. Org. Chem.* **30**, 2983 (1965).

[7] While this work was in progress Mironov[8] *et al.* and McLean and Haynes[9] reported an extensive study on the preparation and isomerization of mono- and polymethyl-substituted cyclopentadienes.

[8] V. A. Mironov, E. B. Sobolev and A. N. Elizarova, *Tetrahedron* **19**, 1939 (1963) and earlier work refered to therein.

[9] [a] S. McLean and P. Haynes, *Tetrahedron* **21**, 2313 (1965); [b] *Ibid.* **21**, 2329 (1965); [c] *Ibid.* **21** 2343 (1965).

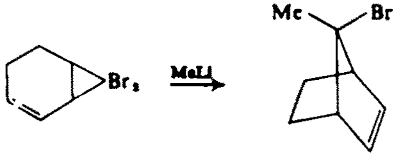
[10] V. A. Mironov, T. M. Fadeeva, E. V. Sobolev and A. N. Elizarova, *J. Gen. Chem. U.S.S.R.* **33** 77 (1963).

[11] J. W. deHaan and H. Kloosterziel, *Rec. Trav. Chim.* **84**, 1594 (1965).

change in isomer composition even after heating at 100° (dimers were formed), whereas equilibrium mixtures[8,9] were obtained from the other methyl- and dimethylcyclopentadienes, upon similar treatment.

From the reaction of the cyclopropane derivative VIII a third isomer was obtained. The ratio of this compound to the cyclopentadiene derivative varied with the reaction temperature while the amount of the allenic isomer remained practically constant; at −78° the ratio was ~1:3 and at 0° ~2:3. The compound was isolated by preparative gas chromatography. The ultraviolet maxima at 274 sh., 263, 254 and 247 sh. mμ strongly indicate the presence of a conjugated triene,[12] and the IR spectrum shows bands at 930 and 895 cm^{-1} characteristic of a vinyl group. Catalytic hydrogenation afforded 2,4-dimethylhexane. These results are all in accord with the structure 2,4-dimethyl-1,3,5-hexatriene (IX), which is confirmed by the NMR spectrum. The configuration about the central double bond is not made apparent by the IR or NMR spectra; however, the lack of fine-structure and the relatively low intensity of the UV absorption are indicative of a *cis* configuration,[13] which is further substantiated by the lack of reactivity towards maleic anhydride. The UV spectrum of the ether solution of the total reaction product contains no absorption indicative of the triene IX, whereas in the total distilled product it is present. Hence, this compound is an artifact formed by thermal treatment (distillation, gas chromatography) of the reaction mixture.

In addition to the results summarized in Table 1, the treatment of 7,7-dibromo-[4.1.0]hept-2-ene (X) with methyllithium at −78° in ether yielded surprisingly, 80% of *syn*-7-bromo-7-methylnorbornene (XI), on the basis of spectroscopic evidence.



X XI

The *syn* configuration was assigned because the compound was recovered unchanged after a methanol solution had been heated under reflux for several hours. It is a fact that *anti*-7-norbornenyl *p*-toluensulfonate solvolyzes 10^7 times faster than the *syn*-isomer,[14] and also that *syn*-7-bromonorbornene is very unreactive.[15]

Reactions of the bicyclopropyl derivatives with methyllithium were carried out as described for the vinylcyclopropanes. Allenic compounds were encountered in the reaction products and in one instance as the exclusive product; the reaction of the bromide XII afforded the crystalline diallene 2,7-dimethyl-2,3,5,6-octatetraene (XIII) in 92% yield. Besides strong allenic absorption at 1970 cm^{-1}, the compound exhibits an intense maximum at 213 mμ (ε 41,500), consistent with the conjugated diallene structure. The NMR spectrum confirmed the assignment. As expected,[16]

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[12] 2,5-Dimethyl-1,3,5-hexatriene absorbs at 272, 261, and 252 mμ, see K. Alder and H. von Brachel, *Liebigs. Ann.* **608**, 195 (1957).

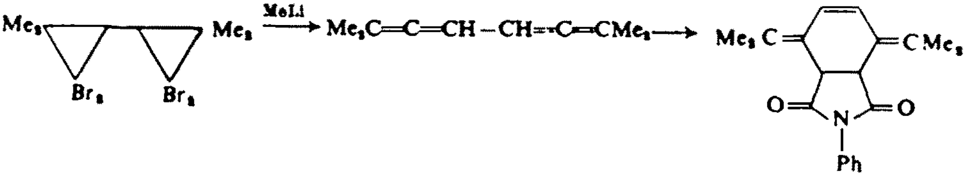
[13] E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 329. McGraw-Hill, New York (1962).

[14] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* **77**, 4183 (1956).

[15] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.* **76**, 4072 (1954).

[16] Conjugated vinyl allenes react with maleic anhydride, see A. V. Fedorova and A. A. Petrov, *J. Gen. Chem. U.S.S.R.* **32**, 3471 (1962) and Refs. therein.

the diallene reacted with N-phenylmaleimide to give compound XIV, characterized by elemental analysis and spectroscopic evidence. Reaction of XIII with methyl acetylenedicarboxylate also took place, but the adduct could not be isolated. Longer reaction time was required in this case and a considerable amount of other material, some polymeric, was formed. Further chemical evidence for structure XIII is provided by its thermal reaction to yield 3,4-diisopropylidenecyclobutene.[17] A few conjugated diallenes have been reported in the literature.[18] The present synthesis, however, certainly represents the most convenient route to a member of this class of compounds since the overall yield of XIII from 2,5-dimethyl-2,4-hexadiene is more than 80%.



XII XIII XIV

The reaction of *trans*, *trans*-3,3′-dimethyl-2,2,2′,2′-tetrabromobicyclopropyl (XV) took a very different course. As the first drops of methyllithium solution were added, the reaction mixture attained a yellow color, which persisted and grew more intense as the reaction proceeded. The ultraviolet spectrum of the ether solution exhibited maxima at 253·5 and 355 mμ, the latter being broad and causing the yellow color. Distillation provided only a small amount of a liquid, λ_{max} 213 (ε 8800), 255 (ε 12500) and 350 mμ (ε 240). The first maximum belongs most probably to the diallene 2,3,5,6-octatetraene as also evidenced by an infrared band at 1960 cm^{-1}. The other maxima belong to the main product *viz.* 2,6-dimethylfulvene (XVI). The NMR spectrum shows complex olefinic absorption in the τ 3·5–4·4 region. The methyl group attached to the ring gives rise to a singlet at τ 8·02. Another peak at τ 7·88 is part of a doublet, the other part being partly obscured by the above singlet; consequently, this resonance must be due to the exocyclic methyl group, coupled ($J = 6$ c/s) by the adjacent proton. The ratio of olefinic to saturated protons is approximately 2:3, consistent with the structure XVI; the data available, however, do not distinguish between the two possible stereoisomers of the fulvene. Catalytic hydrogenation afforded a stereoisomeric mixture of 1-ethyl-3-methylcyclopentane. Similarly, from 1,1′-dimethyl-2,2,2′,2′-tetrabromobicyclopropyl (XVII) and methyllithium 1,2-dimethylfulvene (XVIII) was obtained as the sole volatile product. As in the preceding case, the structure was established on the basis of spectroscopic evidence and identification of the hydrogenation product as a stereoisomeric mixture of 1,2,3-trimethylcyclopentanes. The yields of volatile compounds from both these reactions were rather low and variable, the residues being polymer-like material. This is not surprising considering the general instability of fulvenes.[19] Only a small amount of 2,2,2′,2′-tetrabromobicyclopropyl was available, but preliminary results indicate that a mixture

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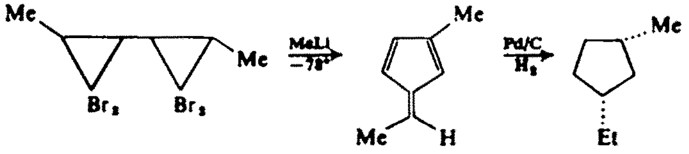
[17] L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.* **87**, 4506 (1965).

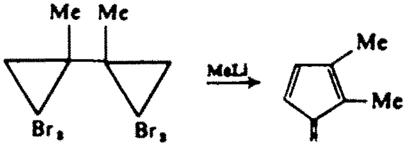
[18] F. Bohlmann and K. Kieslich, *Chem. Ber.* **87**, 1363 (1854); R. Kuhn and H. Fischer, *ibid.* **94**, 3060 (1961); L. Groizeleau-Miginiac, *C.R. Acad. Sci., Paris*, **248** 1190 (1959).

[19] For a review of fulvenes, see K. Häfner, K. H. Häfner, C. Konig, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem.* (Int. Ed.) **2**, 123 (1963); see also H. Schaltegger, M. Neuenschwander and D. Meuche, *Helv. Chim. Acta* **48**, 955 (1965).

of fulvene and an allene, probably 1,2,4,5-hexatetraene, was formed by reaction with methyllithium. Unfortunately, the bromide is not readily available[8] and further work on this reaction is not contemplated.



XV XVI

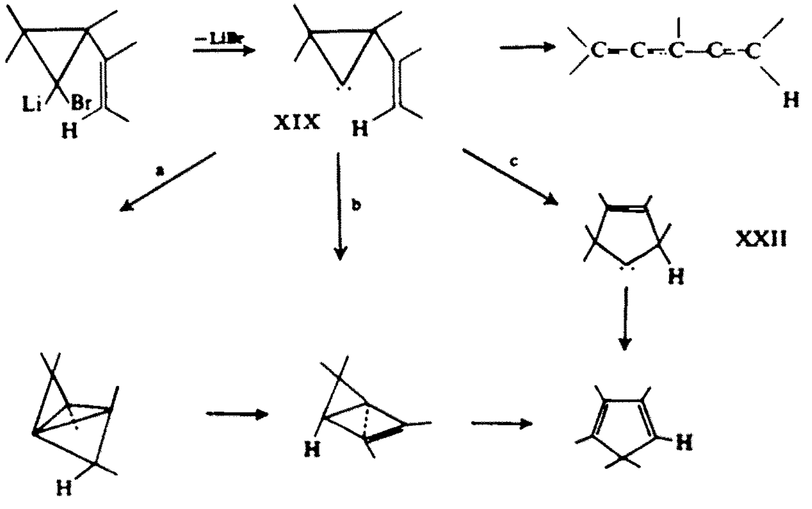


XVII XVIII

DISCUSSION

The deep-seated rearrangement taking place in the reaction leading to the cyclopentadienes (or fulvenes) may be rationalized in a number of ways. For simplicity let us consider the reaction as involving a carbene (cyclopropylidene) intermediate,[20] generated from the lithio-bromo compound by elimination of lithium bromide. This intermediate (XIX) could then undergo ring-opening to the allene, a well substantiated reaction,[4,20] or react intramolecularly with the double bond. The latter reaction would have to lead to the cyclopentadienes since an allene-cyclopentadiene isomerization appears highly unlikely, particularly under the present reaction

Chart I



XX XXI

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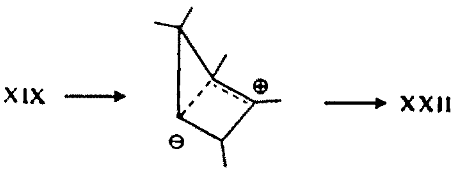
[20] For general reviews on carbene chemistry, see W. Kirmse, *Carbene Chemistry* Academic Press, New York, N.Y. (1964); J. Hine, *Divalent Carbon*. Ronald Press, New York, N.Y. (1964).

conditions. In Chart I three reaction paths which might yield cyclopentadienes are depicted. Addition to the double bond, according to path a, would give the unprecedented tricyclopentane derivative XX. A crude estimate of the strain energy in this molecule can be obtained by adding the strain energy of a bicyclobutane[21] to that of cycloropane (27 kcal/mole) which results in about 90 kcal/mole. This is minimum value,[21] 100–110 kcal/mole being probably a more realistic figure. Except for this extra strain energy, as compared with bicyclobutane, there is no other apparent driving force that would significantly enhance its thermal reorganization. Consequently it seems possible that tricyclo[2.1.0.0^{2,4}]pentane might be thermally stable at −78°. However, if a rearrangement were to take place under the reaction conditions, the bicyclo[2.1.0]pentene isomer (XXI) might conceivably be formed, although the thermal rearrangement of various bicyclobutanes gives no evidence of 1,3-bond cleavage.[22] Compound XXI would also be the product from intramolecular insertion into an olefinic CH bond (path b). The latter is, however, an unlikely path since 2,5,5-trimethylcyclopentadiene is the main product from the bromide VIII, in which no olefinic hydrogens are available for insertion. The bicyclopentene would be expected to rearrange thermally to the corresponding cyclopentadiene. Bicyclo-[2.1.0]pent-2-ene has recently[23] been obtained by photolysis of cyclopentadiene, which indeed was reformed on thermolysis. Therefore, the stability of bicyclopentene[24] combined with the failure to obtain evidence for the presence of the compounds (XXI) in any of the reaction mixtures renders this mechanistic route doubtful.

It is well established that vinylcyclopropanes undergo thermal isomerization to cyclopentenes.[25] Formally, such a process would lead from XIX to a new carbene XXII (path c), which by insertion into an adjacent CH bond would yield the cyclopentadiene. The fact that the present rearrangement takes place below room temperature, while 300–500° is normally required for a vinylcyclopropane, almost demands that different mechanisms are operating in the two cases. In the present reaction bond formation between the double bond and the electron deficient carbon would be a very likely first step. The cyclopropylcarbinyl type system formed could result in



the carbene XXII. These reorganizations would have to be very fast (faster than ring opening to the allene) and the total picture would be that of a concerted rearrangement.

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[21] R. B. Turner, P. Goebel, W. von E. Doering and J. F. Coburn, *Tetrahedron Letters* 997 (1965) have estimated the strain energy of 1,3-dimethylbicyclobutane to 67 kcal/mole.

[22] E. P. Blanchard and A. Cairncross, *J. Amer. Chem. Soc.* **88**, 487 (1966), and references therein; see however, I. A. D'yakonov, V. V. Razin and M. I. Komandantov, *Tetrahedron Letters* 1135 (1966).

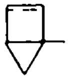
[23] J. L. Brauman, L. E. Ellis and E. E. van Tamelen, *J. Amer. Chem. Soc.* **88**, 846 (1966).

[24] At room temperature a dilute solution of bicyclopentene possesses a half-life of about 2 hr.[23]

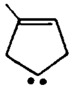
[25] E. Vogel, R. Palm and K. H. Ott, *Angew Chem.* **72**, 21 (1960); C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.* **82**, 1007 (1960).

Based on the above considerations, path c appears to be the preferred route, while path b is definitely ruled out. In the following, the different methylcyclopentadiene isomer mixtures obtained from the reactions of compounds IV and V[26] (Table 1) will be discussed in terms of path a and c. By the former route IV would be expected to yield a mixture of bicyclopentenes, in which XXIII would predominate over XXIV; consequently, 2-methylcyclopentadiene should be the main product by valence isomerization, contrary to what was observed. Similarly, in the case of V approximately equal amounts of 1- and 2-methylcyclopentadiene would be expected, while actually the 2-isomer predominated. On the other hand, the reaction of IV by way of

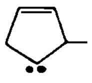
XXIII



XXIV



XXV



XXVI

the carbene XXV, would be expected to yield approximately equal amounts of the two isomers, close to what was observed. The reaction of compound V by the same path would give the carbene XXVI. On the assumption that the rate of insertion is about four times faster[20,27] into a *tert* versus a *sec* C—H bond, 2-methylcyclopentadiene should predominate by a factor of about two, in reasonable agreement with the experimental results, It should be pointed out that the 5-isomer, expected by insertion into the *sec* C—H bond, is thermally unstable, isomerizing to the 1-isomer,[8,9a,b] No mechanistic preference is provided by the results from compounds VI and VII; 2,5-dimethylcyclopentadiene expected to be formed from VII by either route, would rearrange to a mixture of the 1,3- and 1,4-isomers, the products actually observed.

The formation of the norbornene derivative XI from X is readily explained by path c. There are many ways by which XI could be formed from the rearranged carbene, for instance by insertion into methyl bromide, but the apparent stereospecificity remains unexplained.

The formation of the fulvenes fits mechanistically well into the general concept as demonstrated below in the case 2,6-dimethylfulvene (XVI). It is necessary and reasonable to assume that an allenic bond is first formed from one of the cyclopropane rings. The compound thus formed (XXVII) would react further with rearrangement to the fulvene.

It is clear that the reaction of compound XII cannot possibly lead to a fulvene by either route, but the exclusive formation of the diallene XIII is nevertheless surprising. This can be understood, however, on the condition that methyl substituents on a ring carbon other than that bearing the unsaturated group (alkenyl or allenyl) enhance

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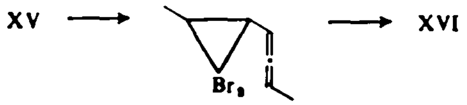
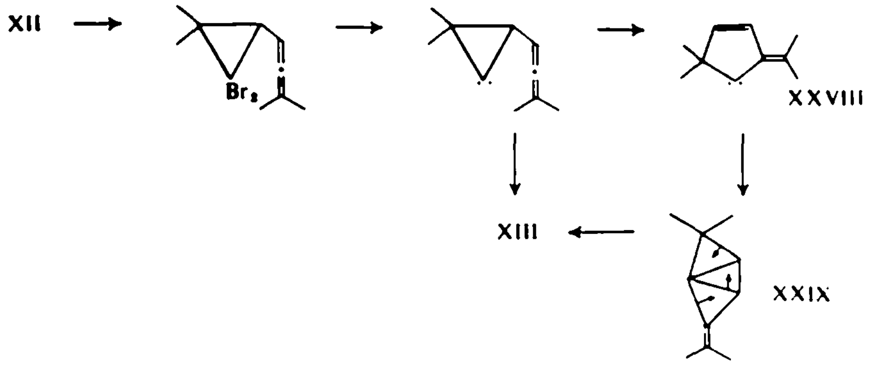
[26] Compound V consists actually of two isomeric bromides but both would give the same carbene or tricyclic intermediate with methyllithium.

[27] J. H. Knox and A. F. Trotman-Dickenson, *Chem. & Ind.* 731 (1957).



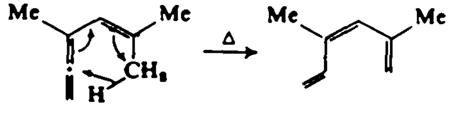
XXVII



the rate of ring opening. Examining Table 1, it is perhaps significant that bromide VII afforded 32% of the respective allenic product and that 1,1-dibromo-2,2-dimethyl-3-isopropenylcyclopropane, present in compound XIII to maximum 10%, yielded 7% of the corresponding allene. On the other hand, practically no allene was obtained from VI, suggesting the importance of the site of substitution.[28]

There are other ways of explaining the exclusive diallene formation, but they are hardly more convincing. If the carbene XXVIII were formed, addition to the endocyclic double bond would give the tricyclic compound XXIX, which would also be the compound expected by path a (Chart 1). The fact that one can visualize the collapse of XXIX to the diallene (but not to a fulvene) is interesting. With such a mechanism it is hard to accommodate the fact that no products from either CH insertion or interaction with the exocyclic double bond of XXVIII were encountered.

The reaction product obtained from the bromide VIII requires an explanation. As mentioned above, the starting material is invariably contaminated with some (<10%) of the isomer, 1,1-dibromo-2,2-dimethyl-3-isopropenylcyclopropane,[3] which with methyllithium would yield 2,5-dimethyl-1,3,4-hexatriene and 2,5,5-trimethylcyclopentadiene, the compounds isolated. Similarly, from compound VIII besides



XXX IX

the above cyclopentadiene, 3,5-dimethyl-1,2,4-hexatriene (XXX) would be an expected product. The latter was not isolated, but it probably isomerized thermally by 1,5-hydrogen migration to the triene IX.[30] Such a mechanism requires the *cis*-configuration

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[28] The relative rates of thermally induced ring opening of various methyl-substituted 1,1-dichloro-2-ethoxycyclopropanes are interesting in this connection. A *cis* methyl group at the 3 position causes a 19 fold rate increase whereas substitution at the 2-position has little effect.[29]

[29] L. Skattebøl, *J. Org. Chem.* 31, 1554 (1966).

[30] Crowley[6d] has found that 2,5-dimethyl-2,3,5-octatriene rearranged rapidly at 115° to 2,5-dimethyl-2,4,6-octatriene; see also Mikolajczak *et al.*[6e] for another example of this rearrangement.

of IX, in agreement with experimental results. Obviously, 2,5-dimethyl-1,2,4-hexatriene could not undergo this rearrangement.

On the basis of the above arguments it seems likely that path c is responsible for the cyclopentadiene (fulvene) formation. This certainly does not mean that a free carbene is produced in the reaction; the experimental results do not distinguish between that, a carbenoid, or an α-halolithium intermediate as the actual isomerizing species. Indeed, the stereoselective formation of *syn* XI suggests that the electron deficient carbon is complexed with lithium bromide and/or methyl bromide. It is hoped that further work will help to clarify the mechanism of this interesting rearrangement.

EXPERIMENTAL[21]

General procedure. The reactions were carried out as described.[1] The ether solns of the total reaction products were analyzed by GLPC. Because of the extreme tendency of the cyclopentadienes and fulvenes to dimerize, the ether was usually only partly evaporated and pure samples of the components were obtained by preparative GLPC; when not otherwise stated a 15 ft. Apiezone L on Chromosorb W column was used.

Cyclopentadiene and 1,2,4-*pentatriene*

Reaction of III with MeLi gave a mixture of two isomeric compounds. These were isolated by preparative GLPC, and the major component (86%) was identified as 1,3-cyclopentadiene by comparison with an authentic sample. The minor component (14%) was shown to be 1,2,4-pentatriene also by comparison with an authentic sample.[22]

Methylcyclopentadiene. (a) The liquid product obtained from the reaction of IV and MeLi was shown to consist of 3 compounds in a ratio of 17:35:48. The minor component was separated by preparative GLPC and shown to be 3-methyl-1,2,4-pentatriene; ν_{max} 1940, 850 (—C═C═CH$_2$) and 1610, 988, 895 cm^{-1} (—CH═CH$_2$). The two major components were separated together, n_D^{22} 1·4576, and identified as a mixture of 1- and 2-methylcyclopentadiene by comparison with an authentic sample, prepared from commerically available methylcyclopentadiene dimer. The 1-isomer predominated in the original reaction mixture.

(b) The product obtained from a mixture of 1,1-dibromo-2-methyl-3-vinylcyclopropane and 1,1-dibromo-2-(2-propenyl) cyclopropane[3] and MeLi was shown to consist of 85% methylcyclopentadienes and 15% allenic compounds. On the basis of GLPC retention times on both dimethyl sulfolane[7,8a] and β,β′-oxydipropionitrile columns the cyclopentadiene fraction consisted of 71% of the 2-methyl and 14% of the 1-methyl isomer.

1,2-*Dimethylcyclopentadiene*

The reaction of VI with MeLi gave essentially (98%) 1,2-dimethylcyclopentadiene, b.p. 58–59° (150 mm), n_D^{24} 1·4580; λ_{max} 251·5 mμ (ε 3400); ν_{max} 1630, 1590, 685 cm^{-1} (—C═C—); NMR spectrum shows 3 multiplets at 3·95 (C═C—H), 7·28 (—CH$_2$) and 8·25 (—CH$_3$) with peak area ratio 1:1:3, respectively. (Found: C, 88·94; H, 10·65. Calc. for C_7H_{10}: C, 89·29; H, 10·71%.)

The yield of distilled product was only 49% because dimerization took place during the distillation. The other product (< 2%), formed in the reaction, was not obtained pure, but the IR absorption at 1940 cm^{-1} indicates the structure 3,4-dimethyl-1,2,4-pentatriene for this compound.

The maleic anhydride adduct was obtained in the usual way in 83% yield. The compound was obtained as colorless needles from ether–benzene, m.p. 91°. The structure was determined as 1,6-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride; ν_{max} 1850, 1775 ((CO)$_2$O) 1620 cm^{-1} (C═C). The NMR spectrum shows a multiplet at 4·12 (C═C—H), complex absorption

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[21] B.ps and m.ps are uncorrected. IR spectra: on a Beckman IR 5A and IR 10 spectrometer; UV spectra: in n-heptane soln, when not otherwise stated, on a Cary Model 14 spectrometer; NMR spectra: on a Varian A 60 instrument with CCl_4 as solvent and Tms as internal standard. The chemical shifts are given in τ values. Preparative scale gas chromatographic separations were carried out with a Wilkins Autoprep Model A 700 instrument.

[22] E. R. H. Jones, H. H. Lee and M. C. Whitting, *J. Chem. Soc.* 341 (1960).

in the 6·25–6·9 region (—CH), a doublet at 8·28 (C═C—CH$_3$), a broad singlet at 8·47 (—CH$_3$) and superimposed on the last bands, absorption due to the methylene groups. (Found: C, 68·91; H, 6·44. Calc. for $C_{11}H_{12}O_2$: C, 68·73; H, 6·29%.)

The N-*phenylmaleimide adduct* was obtained in the usual way in 82% yield, m.p. 127–128°. Sublimation and recrystallization gave pure adduct, m.p. 128° (lit.[26] 122–123°); NMR: s. 8·51 (CH$_3$, CH$_3$) d. 8·32 (C═C—CH$_3$), unresolved multiplet 4·27 (C═CH), and complex absorption in the 2·6–3·1 region (arom.) and 6·6–7·3 region (CH); the peak area ratio 5:3:1:3:5, respectively. (Found: C, 76·38; H, 6·61; N, 5·31. Calc. for $C_{17}H_{17}O_2N$: C, 76·88; H, 6·41; N, 5·24%.)

Dimethylcyclopentadienes and trans-2,3,5-*heptatriene*

The reaction of VII and MeLi yielded a liquid consisting of essentially 3 compounds in a ratio of 47:21:32. The two first compounds had very similar retention times on both β,β'-oxydipropionitrile and dimethylsulfolane columns at 25°. They were isolated together by preparative GLPC, n_D^{25} 1·4526; λ_{max} 252 mμ (ε 4200) (lit.[32] for 1,3-dimethylcyclopentadiene, n_D^{25} 1·4574; λ_{max} (MeOH) 248·5 mμ); ν_{max} 3025, 1650, 885, 725 cm^{-1} (C═C). The NMR spectrum shows clearly that a mixture of 1,3- and 1,4-dimethylcyclopentadienes is present. Peaks centered at 8·05 and 7·30 are due to Me and CH$_2$ groups, respectively. The olefinic protons give rise to two poorly resolved multiplets at 4·32 and 4·12, due to olefinic hydrogens α and β to the CH$_2$ group, respectively, with peak area ratio of about 5:9, corresponding to about 72% of the 1,3-isomer, in good agreement with the GLPC results.

The mixture reacted with N-phenylmaleimide in the usual way to give a crude solid, from which the adduct of 1,3-dimethylcyclopentadiene was obtained after several recrystallizations from n-heptane, m.p. 104–106° (lit.[32] 100–101°). The NMR spectrum shows a singlet at 8·46 (Me) and a doublet at 8·22 (C═C—CH$_3$); the bridge CH$_2$ absorption is partly obscured by these peaks. Complex absorption centered at 6·90 and 2·70 is due to the *tert* hydrogens and aromatic protons, respectively. The olefinic proton gives rise to a broad singlet at 4·47. (Found: C, 76·51; H, 6·35; N, 5·15. Calc. for $C_{17}H_{17}O_2N$: C, 76·38; H, 6·41; N, 5·24%.)

The third component was also isolated by preparative GLPC and shown to be *trans*-2,3,5-heptatriene, n_D^{25} 1·4922; ν_{max} 1945 (C═C═C), 967 cm^{-1} (*trans* C═CH); λ_{max} 219 mμ (ε 25,400); NMR shows two complex multiplets centered at 8·30 (CH$_3$—C═C) and 4·50 (C═CH) with peak area ratio approximately 3:2.

2,5,5-*Trimethylcyclopentadiene*, 2,5-*dimethyl*-1,3,4-*hexatriene and* 2,4-*dimethyl*-1,3,5-*hexatriene* (IX)

Reaction of VII with MeLi at −78° gave in 82% yield a mixture of essentially 3 compounds. The major component (70%) was separated by fractional distillation and proven to be 2,5,5-trimethylcyclopentadiene, b.p. 56–57° (170 mm), n_D^{24} 1·4334; ν_{max} 3020, 1640, 1610, 795, 722 cm^{-1} (C═C); λ_{max} 250 mμ (ε 2800); NMR: singlet (8·90 (CH$_3$), doublet 8·14 (CH$_3$—C═C), and multiplet 4·28 and 3·38 (C—CH); the peak area ratio is 6:3:1:2, respectively.

The maleic anhydride adduct was obtained in the usual way as a viscous oil, which upon hydrolysis yielded the corresponding diacid, 2,7,7-trimethylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid, m.p. 171° (dec) (lit.[33] m.p. 181° (dec)). (Found: C, 64·52; H, 7·35. Calc. for $C_{12}H_{16}O_4$: C, 64·27; H, 7·19%.)

The N-*phenylmaleimide* adduct was formed in 85% yield and recrystallized from n-heptane. m.p. 128°. (Found: C, 76·97; H, 6·87; N, 4·95. Calc. for $C_{18}H_{19}O_2N$: C, 76·84; H, 6·81; N, 4·98%.)

The two other components could only be separated by preparative GLPC. The minor component (7%) was shown to be 2,5-dimethyl-1,3,4-hexatriene, n_D^{24} 1·4765; ν_{max} 1955 (C═C═C), 1620, 880 cm^{-1} (—C═CH$_2$); λ_{max} 220 mμ (ε 24000). The NMR spectrum shows a multiplet at 4·11, with J = 3·0c/s. characteristic of the CH$_3$—C═C═CH-system;[34] a multiplet at 5·05 is due to the methylene protons, and three peaks centered at 8·21 are caused by the Me groups; the ratio of olefinic to saturated protons is 1:3.

The third component was identified as 2,4-dimethyl-1,3,5-hexatriene, n_D^{24} 1·4885; ν_{max} 3085, 1625, 1590 (C═C), 995, 895 (—CH═CH$_2$), 855 cm^{-1} (C═CH—); λ_{max} 202·5 (ε 1400), 247 sh, (13600), 254 (15400), 263 (14800) and 274 sh (9900). The vinyl group is recognized in the NMR spectrum by the characteristic quadruplet, the X part of an ABX system, centered at 2·98 and complex absorption

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[33] A. Auterinen, *Suomen Kemistilehti* 27B, 29 (1954).

[34] E. I. Snyder and J. D. Roberts, *J. Amer. Chem. Soc.* **84**, 1582 (1962).

in the 4·2–5·2 region; a triplet at 2·17 is due to the Me groups. The ratio of olefinic to saturated protons is 1:1.

Hydrogenation of a mixture of the allene and the triene in pentane solution over a Pd/C catalyst gave as the sole product 2,4-dimethylhexane n_D^{24} 1·3919, identical with an authentic sample.

2,6-*Dimethylfulvene* (XVI)

Reaction of XV with MeLi at −78° in the usual way produced a yellow-colored ether solution which absorbed at 253·5 and 355 mμ. Evaporation of the solvent through a column under reduced press and below room temp with subsequent distillation of the residue at 10^{-3} mm gave a small amount of a liquid, n_D^{24} 1·5198; ν_{max} 1960 (C=C=C) 1650, 1590, 900, 845, 790 cm^{-1} (C=C) λ_{max} 255 (ϵ 12,500) and 350 mμ (ϵ 240), and a peak at 213 mμ (ϵ 8800) which is probably due to the diallene, 2,3,5,6-octatetraene.

Hydrogenation of the liquid in pentane over 5% Pd/C catalyst gave one major product which was separated by preparative GLPC, n_D^{24} 1·4132, and found to be identical with a synthetic stereoisomeric mixture of 1-ethyl-3-methylcyclopentane.[25]

1,2-*Dimethylfulvene* (XVIII)

Reaction of XVII with MeLi at −78° resulted in a deep yellow-colored soln. Evaporation of the ether under reduced press and subsequent distillation of the residue, into a cooled (−78°) flask, afforded a small amount of a yellow liquid, n_D^{24} 1·5104; λ_{max} 242·5 (ϵ 8500) and 376 mμ (ϵ 220); ν_{max} 3030, 1650, 1610, 910 and 755 cm^{-1} (C=C). Thd NMR spectrum shows a singlet at 8·14 due to the Me groups. The methylene protons give rise to a broad doublet at 4·50, and the ring protons show a multiplet centered at 3·96; the peak area ratio is 3:1:1.

Hydrogenation of a pentane soln of the fulvene over 5% Pd/C catalyst gave a mixture of stereoisomeric 1,2,3-trimethylcyclopentanes, n_D^{24} 1·4230, identical with that of an authentic sample.[26]

2,7-*Dimethyl*-2,3,5,6-*octatetraene* (XIII)

Reaction of XII with MeLi afforded XIII in 93% yield after recrystallization from MeOH m.p. 46°; ν_{max} 1970 cm^{-1} (C=C=C); λ_{max} 213 mμ (ϵ 41500); NMR: multiplets 8·32 (CH_3—C—C) and 4·67 (C=HC) with peak area ratio 6:1. (Found: C, 89·62; H, 10·40. Calc. for $C_{10}H_{14}$: C, 89·49; H, 10·51%.)

The N *phenylmaleimide adduct* (XIV) was obtained by refluxing a benzene soln of equimolar amounts of the allene and N-phenylmaleimide for 16 hr. The yield was 82% of product, m.p. 116–120°. Recrystallizations from n-heptane gave pure adduct, m.p. 127–135° (dec); λ_{max} 220 (ϵ 16000) and 287 mμ (ϵ 19500); NMR: singlets of equal intensity at 8·15 and 8·03 (—CH_3), singlet 5·87 (*tert.* CH), singlet 3·69 (C=CH), and multiplet 2·7 (arom.); the peak area ratio is 6:6:2:2:5. (Found: C, 78·03; H, 6·96; N, 4·57. Calc. for $C_{20}H_{21}NO_2$: C, 78·14; H, 6·89; N, 4·56%.)

The compound decomposes by standing.

syn-7-*Bromo*-7-*methylnorbornene* (XI)

The reaction of X[27] with MeLi gave essentially one product, as shown by GLPC. Distillation yielded 80% of XI, b.p. 64° (8 mm), which solidified in the receiver, m.p. 48–50°. In the NMR spectrum of the Me group appears as a singlet at 8·29. The bridgehead protons give rise to a multiplet at 7·18, a triplet at 3·88 is due to the olefinic protons, and the methylene protons show complex absorption centered at 8·95 and 8·17; the last peaks are quite characteristic of a norbornene system.[28] The compound is very volatile, and we were not able to obtain a satisfactory elemental analysis. (Found: C, 50·42; H, 5·80. Calc. for $C_8H_{11}Br$: C, 51·36; H, 5·93%.)

[25] Prepared from 1-ethyl-3-methylcyclopentanol by dehydration with phthalic anhydride, followed by catalytic hydrogenation, b.p. 117–120°, n_D^{24} 1·4148–1·4155.

[26] *Am. Pet. Inst.* IR spectrum no 700, 701.

[27] D. G. Lindsay and C. B. Reese, *Tetrahedron* **21**, 1673 (1965).

[28] P. Lazlo and P. von R. Schleyer, *J. Amer. Chem. Soc.* **86**, 1171 (1964).