Tetrahedron Vol. 26, pp. 3591 to 3615. Pergamon Press 1970. Printed in Great Britain

THE STEREOCHEMISTRY OF FREE RADICAL ADDITIONS OF ALKYL HALIDES TO ALKENES—1.

BROMODICYANOMETHANE*

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(*Received in Germany* 2 *September* 1969; *Received in the UK for publication* 6 *April* 1970)

Abstract—The chain length of the free radical addition reactions of bromodicyanomethane to cyclohexene (**1a**) and to cyclopentene (**1d**) were found to be 2·3 × 10^2 and 1·6 × 10^3, respectively. The addition reaction shows no specific stereoselectivity. The *Curtin–Hammett* principle is shown to be applicable. Thus the conformation of the transition states can be derived from the observed *trans–cis*-isomer ratios. The results for cyclohexene (**1a**) and 1-methylcyclohexene (**1b**) indicate that the cyclohexyl radicals possess a planar or nearly planar configuration in the transition state.

The stereochemistry of free radical additions of hydrogen bromide,[3, 4] thiols[3, 5, 6] and dinitrogen tetroxide[7, 8] to alkenes has been investigated in detail. In contrast, few systematic studies are available on the synthetically interesting free radical additions of alkyl halides and related compounds.[9, 10]

Only the stereochemistry of the addition of polyhalomethanes to norbornene and other bridged cyclic olefines,[10–14] as well as that of the addition of perfluoroalkyliodides to cycloalkenes[15] is well known. Unfortunately, these are examples of systems with quite specific features, so that no generalizations regarding the stereochemical outcome can be made. Moreover, the stereochemistry of the bromotrichloromethane addition to a series of cycloalkenes has been studied.[16, 17]

In order to decide whether alkyl halides in general add predominantly *trans* to double bonds, as has been shown for hydrogen-bromide[10] and thiols[10] and as suggested for bromotrichloromethane,[16–19] or whether the additions proceed non-selectively, we began investigations using bromodicyanomethane as the alkyl halide component. This system was chosen because earlier studies had shown that under suitable conditions this reagent adds practically stoichiometrically to alkenes. Moreover the configurational assignment of the products can be performed quite easily as shown below. Comparable investigations with polyhalomethanes[20] demonstrated that the information gained from bromodicyanomethane can indeed be generalized for typical alkyl halides.

Addition, separation and configurational assignment of cis/trans *isomers*†

Under irradiation and exclusion of oxygen, bromodicyanomethane adds as smoothly to cyclic‡ to open chain alkenes.[2] Chromatography of the reaction mixture from bromodicyanomethane and cyclohexene (**1a**) yielded two crystalline colorless compounds $C_9H_{10}BrN_2$. They were identified by NMR as the *trans* and *cis* addition

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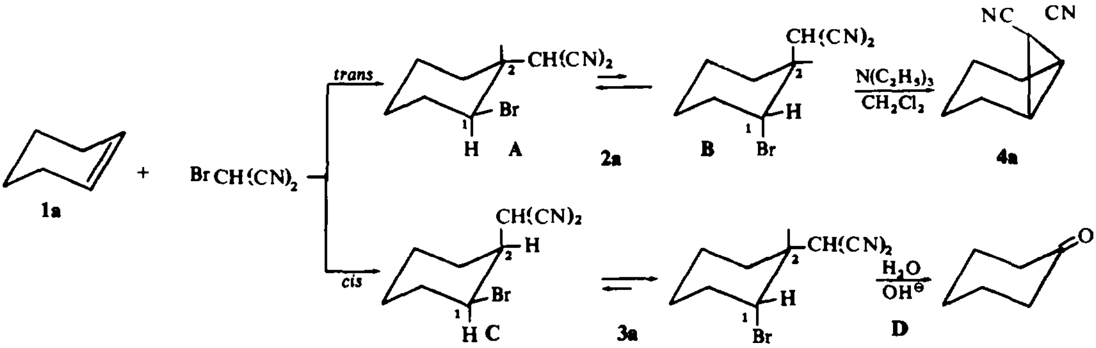
* Part IV on radical additions. Part III loc. cit,[1] Part II loc. cit.[2]

† Preliminary communication loc. cit.[21]

‡ Moreover, as it turned out, carefully purified bromodicyanomethane is necessary to insure smooth reactions; see page 3607.



products: *seqtrans*-1-bromo-2-dicyanomethylcyclohexane[22] (m.p. 56·5°, **2a**) and *seqcis*-1-bromo-2-dicyanomethylcyclohexane (m.p. 68·5°, **3a**): The proton at C1 in the isomer with m.p. 56·5° is predominantly axial (broad signal, strongly split up, centered at δ 3·95 ppm) and in the isomer with m.p. 68·5° it is predominantly equatorial (small band width, δ 4·78 ppm, Fig. 1). Since conformation **D** of the *seqcis* isomer should be of lowest energy,* it follows that the isomer with the C1 proton predominantly axial has the *seqtrans* configuration **2a** (conformation **A** predominantly populated).

The same assignment may be made on the basis of the different chemical behaviour of the isomers towards triethylamine. The addition products of bromodicyanomethane to open-chain alkenes give even with weak bases smooth 1,3-elimination of HBr with formation of 1,1-dicyanocyclopropanes.[2] Of the two addition products resulting from cyclohexene, only one reacted fast and quantitatively (at 20°) to give 7,7-dicyanonorcarane (**4a**); the other isomer (with higher m.p.) remained unchanged even after prolonged reaction. As to be expected, HBr elimination thus occurs via an E1cB mechanism, since in an E1 mechanism with ionization at C1 both compounds should react to form **4a**. Since an E1cB mechanism is accompanied by inversion at C1 (intramolecular substitution), only the *seqtrans* isomer **2a** possesses the steric requirements for the formation of the *cis* bonded 7,7-dicyanonorcarane (**4a**). Thus, the isomer which cyclizes to **4a** corresponds to structure **2a**.† Inspection of appropriate models shows that the intramolecular substitution of bromine by backside attack of the dicyanomethyl anion can only occur in the diaxial conformation **B** or perhaps in a twist-boat conformation of **2a** (see page 3597).

Strong aqueous bases react with **3a** at room temperature to give cyclohexanone. In this reaction **4a** is not an intermediate as assumed by Torssell and Dahlquist,[24] since **4a** is stable in cold dilute alkali and also on heating for a short time. Apparently, **3a** probably in conformation **D**, suffers smooth 1,2 elimination of HBr to form 1-cyclohexenyl-malonodinitrile, which then isomerizes by a base-catalyzed prototropic shift to cyclohexylidenemalonodinitrile. Hydrolysis of the latter affords cyclohexanone.

Compound **4a** is best prepared by shaking a solution of **2a** and **3a** in methylenechloride, after cyclization of **2a** with triethylamine, with aqueous NaOH and removing the cyclohexanone formed from **3a** with hydrogen sulfite. In this manner we obtained **4a** in an overall yield of 38% (with respect to bromodicyanomethane). Treatment of the mixture of **2a** and **3a** with triethylamine followed by distillation of **4a** resulted

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* The torsional angles between bromine and the dicyanomethyl group in **C** and **D** are 60°. The dipole moments therefore hardly differ from one another. For a discussion of the conformational energy of a dicyanomethyl group, see page 3605.

† The configuration of the isomeric 2-chlorocyclohexanols were determined analogously, loc. cit.[23]

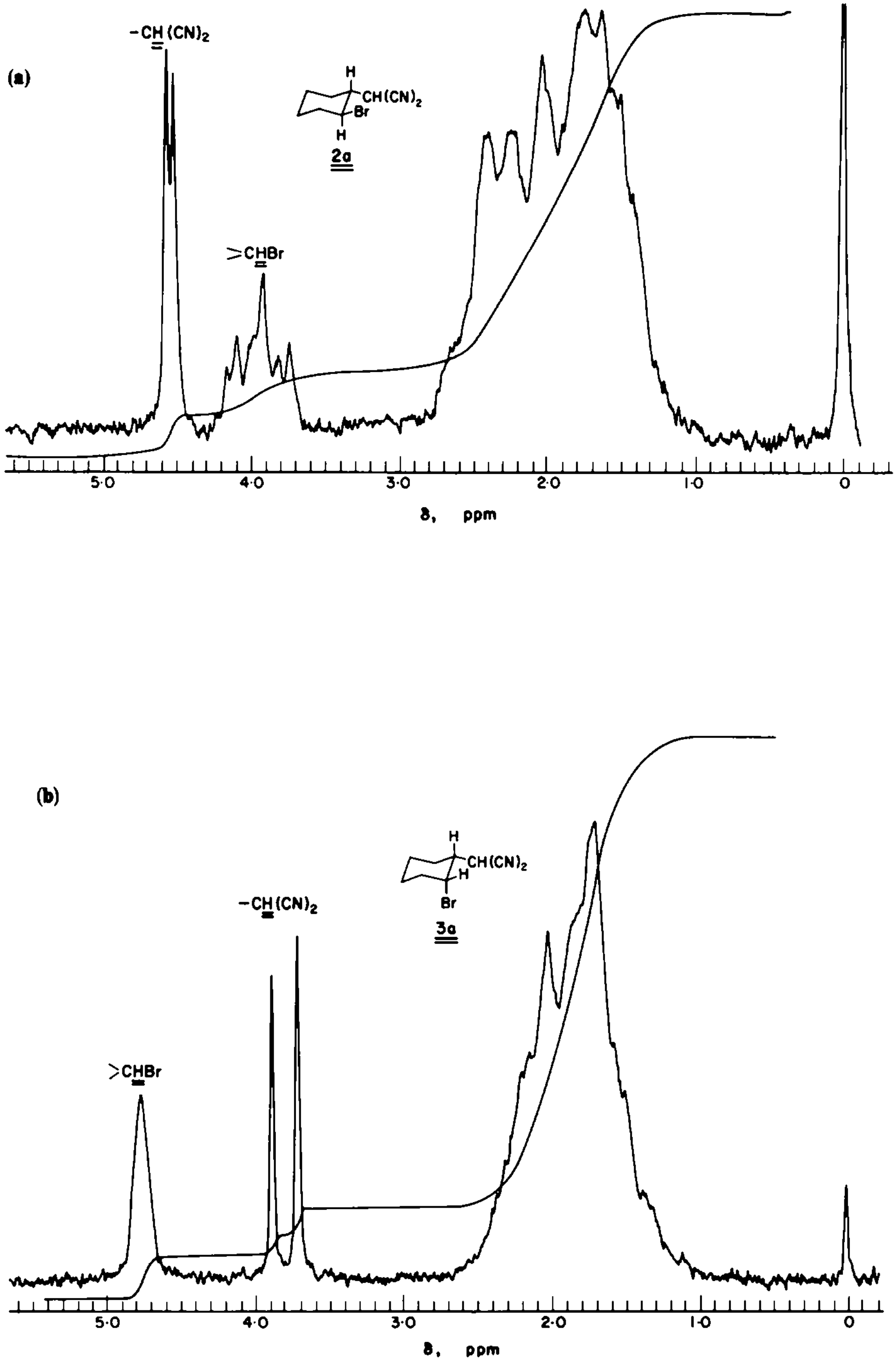


FIG 1. NMR spectrum (60 Mc) of (a) *seqtrans*-1-bromo-2-dicyanomethylcyclohexane (**2a**) and (b) *seqcis*-1-bromo-2-dicyanomethylcyclohexane (**3a**) in carbontetrachloride, TMS internal standard.

in a smaller yield (29%), but **3a** could be obtained (19%) from the residue by recrystallization from ligroin. **2a** was best prepared by fractional crystallization of the mixture of isomers from methanol at − 40° (13% yield).

Perhaps with the exception of **1h**, all cycloalkenes listed in Table 1 could be converted to the *trans* and *cis* addition products in nearly theoretical yields.

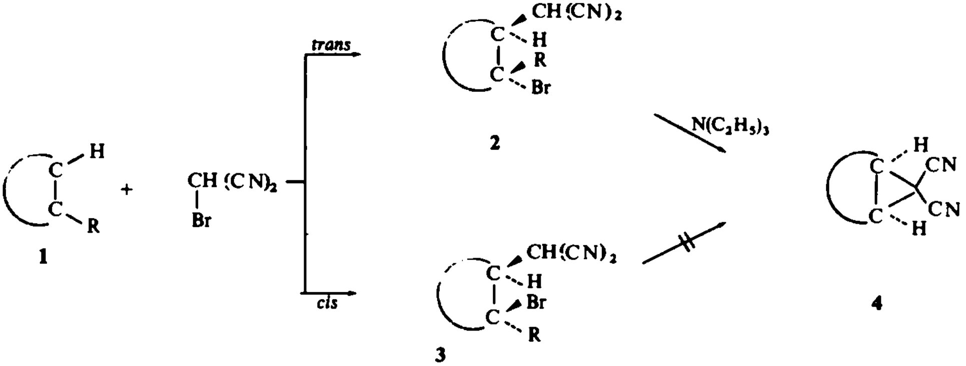
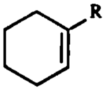
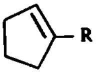
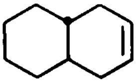
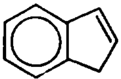


TABLE 1. PRODUCTS AND PRODUCT RATIOS OF THE FREE RADICAL ADDITION OF BROMODICYANOMETHANE TO ALKENES

Alkene 1			*seqtrans*-prod. 2 m.p., yield[b]	*seqcis*-prod. 3 m.p., yield[b]	[*seqtrans*][a] / [*seqcis*]	Cyclopropane 4 m.p., yield[b]
		R				
	1a	H	**2a** (56·5° 13%)	**3a** (68·5°[c] 19%)	1·1	**4a** (62°[d] 38%)
	1b	CH_3	**2b** (79° 56%)	**3b** (53° 16%)	2·2	**4b** (36·5° 53%)
	1c	C_2H_5	**2c** (71° 20%)	**3c** (73° 5%)	1·5	**4c** (liquid 73%)
	**1d**	R = H	**2d** (21·5° 28%)	**3d** (49·5° 6%)	3·8	**4d** (35° 51%)
	1e	R = CH_3	**2e** (40° 38%)	**3e** (44·5° 5·5%)	2·6	**4e** (29·5° 37%)
	**1f**		**2f** (119° 90%)	**3f** — —	~ 27[e]	**4f** (73° 85%)
	**1g**		**2g** (74·5° 2%)	**3g** (49° 12%)	0·28	**4g** (86·5° 5%)
	**1h**	—	— — —	— — —	—	**4h** (96° 10%)

[a] Concerning the determination of the ratio, see page 3611 [b] based on bromodicyanomethane, **4c** based on **2c** [c] Ref[24] 66·5° [d] Ref [24a] 62–63° [e] Based on **2f** and **3f′** (see Scheme 1). Concerning the determination of the isomer ratio, see p. 3597.

Isomers were obtained in pure form either by chromatography or by fractional crystallization. **3d** remained as a residue after treatment of the reaction mixture with triethylamine and distillation.

The addition products of bromodicyanomethane to **1h** could not be isolated in pure form. They decomposed upon chromatography with silica gel. Under such conditions **2h** eliminates HBr and forms 6,6-dicyano-2,3-benzobicyclo[3.1.0]hexene-(2) (**4h**), while **3h**, most likely also by way of 1,2 HBr elimination, yields green products which were not further identified.

As with the adducts from cyclohexene (see page 3592) the *seqtrans* configuration was assigned to all those addition products which afforded dicyanocyclopropanes with triethylamine, the *seqcis* configuration to all those which remained unchanged with triethylamine.

The failure of the *seqcis* isomers (**1b**, c, e) to react shows that under the reaction conditions even the adducts having bromine at the tertiary C-atom do not give 1,3 E1-elimination of HBr. It is noteworthy that even with these compounds smooth (intramolecular) S_N2-reactions take place. To the best of our knowledge. only one other case of an S_N2 reaction at a tertiary alkyl halide has been recorded.[25]

The constitution of compounds **4a–h** is consistent with their elemental analyses. Moreover, that no 1,2-elimination of HBr took place is evidenced by the absence of absorption bands in the region 1550 to 1700 cm^{-1}; further evidence is provided by the absence of an NMR signal above $\delta = 3$ ppm for **4a–g**, as well as by the position and coupling constants of the peaks in the NMR-spectrum of **4h**.

Bromodicyanomethane reacts with *trans*-Δ^2-octalin (**1f**) to give essentially only one product, 2α-Bromo-3β-dicyanomethyl-*trans*-decalin (**2f**), which was isolated in pure form by simple recrystallization from tetrachloromethane. That the substituents are *trans* to each other follows from the smooth HBr-elimination by triethylamine with formation of 4,4-dicyano-tricyclo[5.4.0-*trans*.$0^{3,5}$]undecane (**4f**); the axial position of the substituents follows from the position and half-width of the NMR-signals of the protons at C1 and C2 (Fig 2).[26a]

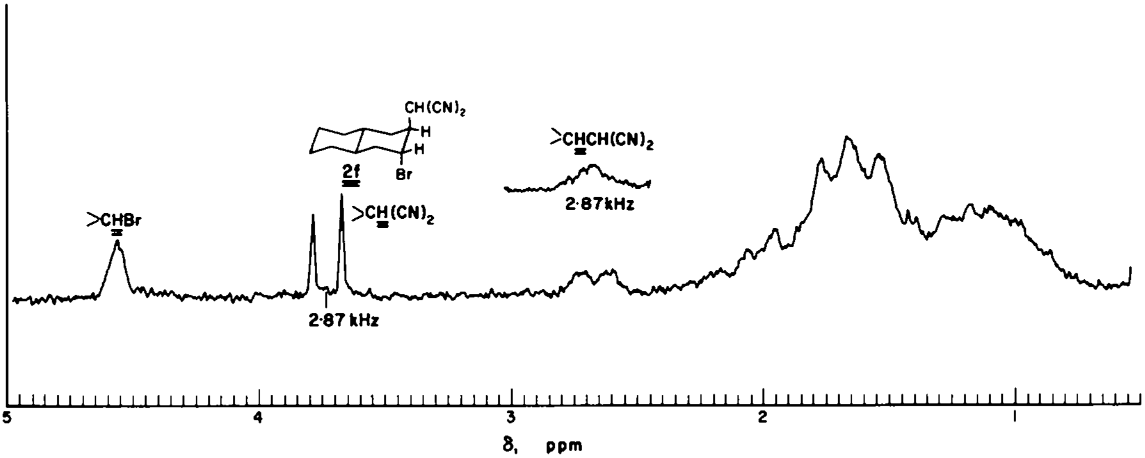
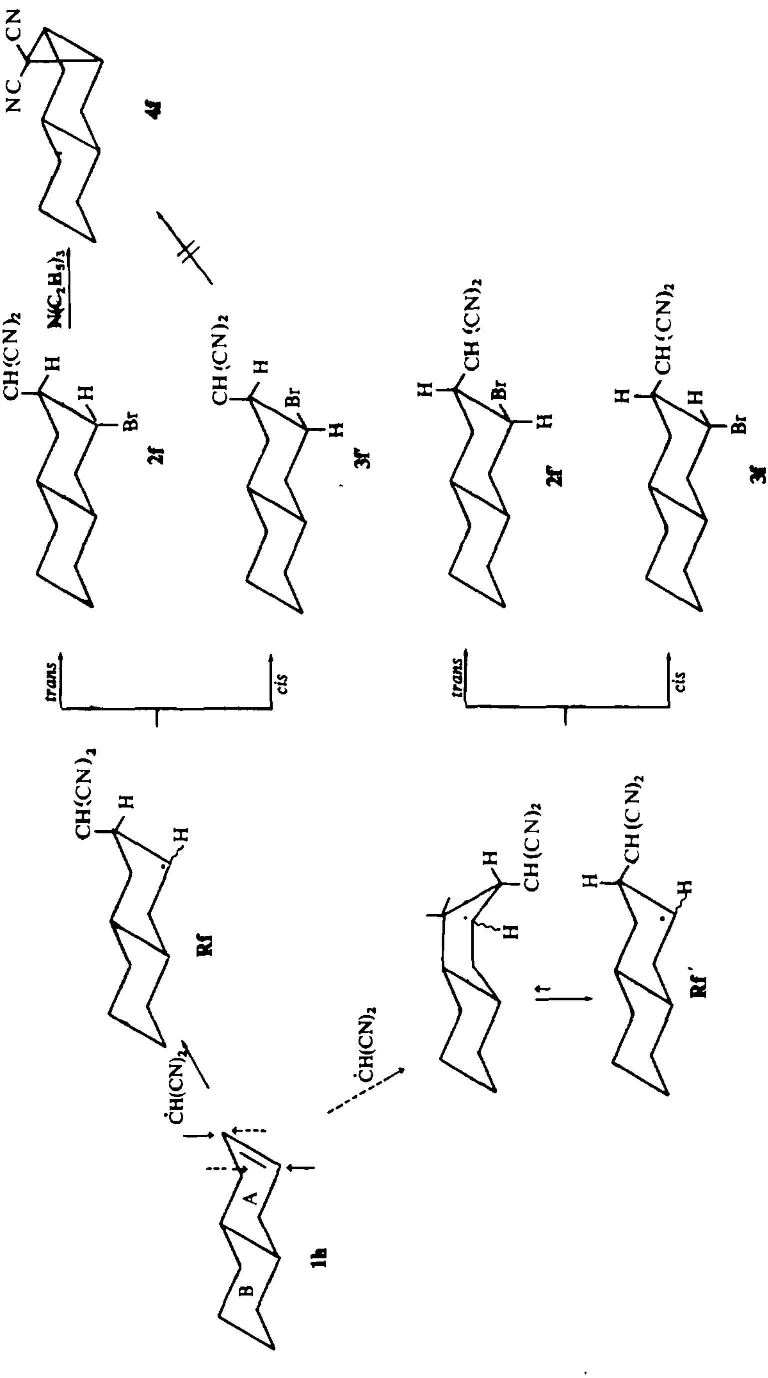


FIG 2. NMR spectrum (100 Mc) of 2α-bromo-3β-dicyanomethyl-*trans*-decalin (**2f**) in tetrachloromethane, TMS internal standard.

In the NMR spectrum of **3a** the signal of the equatorial C1 proton is at 4·78 ppm. (half-width 0·1 ppm, Fig 1). Moreover, due to its equatorial position, the C2 proton of **2f** absorbs at lower fields, so that it may be recognized as a broad doublet ($J = 11·5$ c/s) at 2·77 ppm next to the other peaks of the ring protons. This assignment was substantiated by spin decoupling experiments (irradiation at 2·87kHz).

Evidence for the formation of the three other possible isomers (Scheme 1) the *seqtrans* diequatorial **2f'**, as well as the *seqcis* with equatorial and acial dicyanomethyl groups, **3f'** and **3f**, respectively, cannot be obtained from the NMR spectrum of the original reaction mixture. It is practically identical to that of pure **2f** (Fig. 2). However, upon removal of **2f** from the crude product by triethylamine induced cyclization to **4f** (which shows no absorption above 2·5 ppm), NMR peaks using very concentrated solutions appear which may be assigned to compounds **2f'**, **3f** and **3f'** (Fig. 3).

Scheme 1.


1h
A
B
ĊH(CN)$_2$
Rf
Rf'
trans
cis
trans
cis
2f
3f
2f'
3f'
4f
N(C$_2$H$_5$)$_3$
CH(CN)$_2$
H
Br
NC
CN

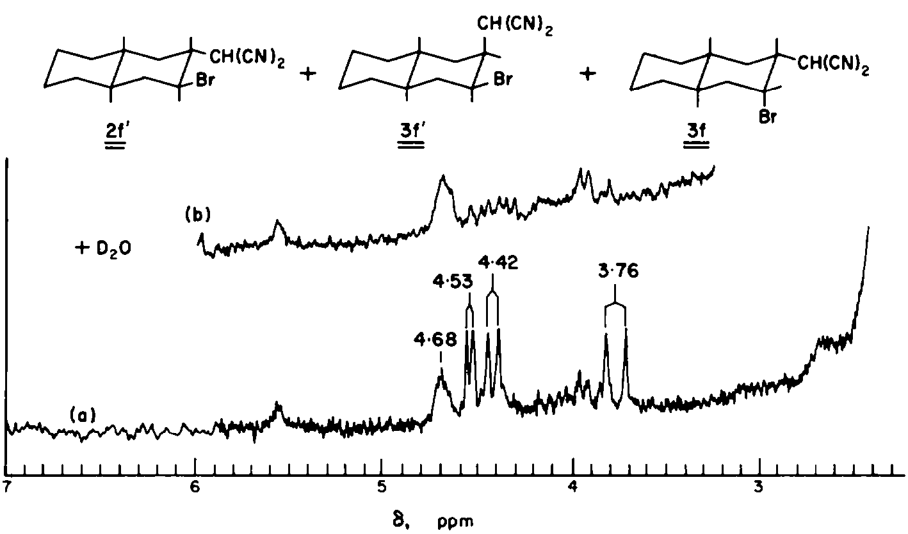
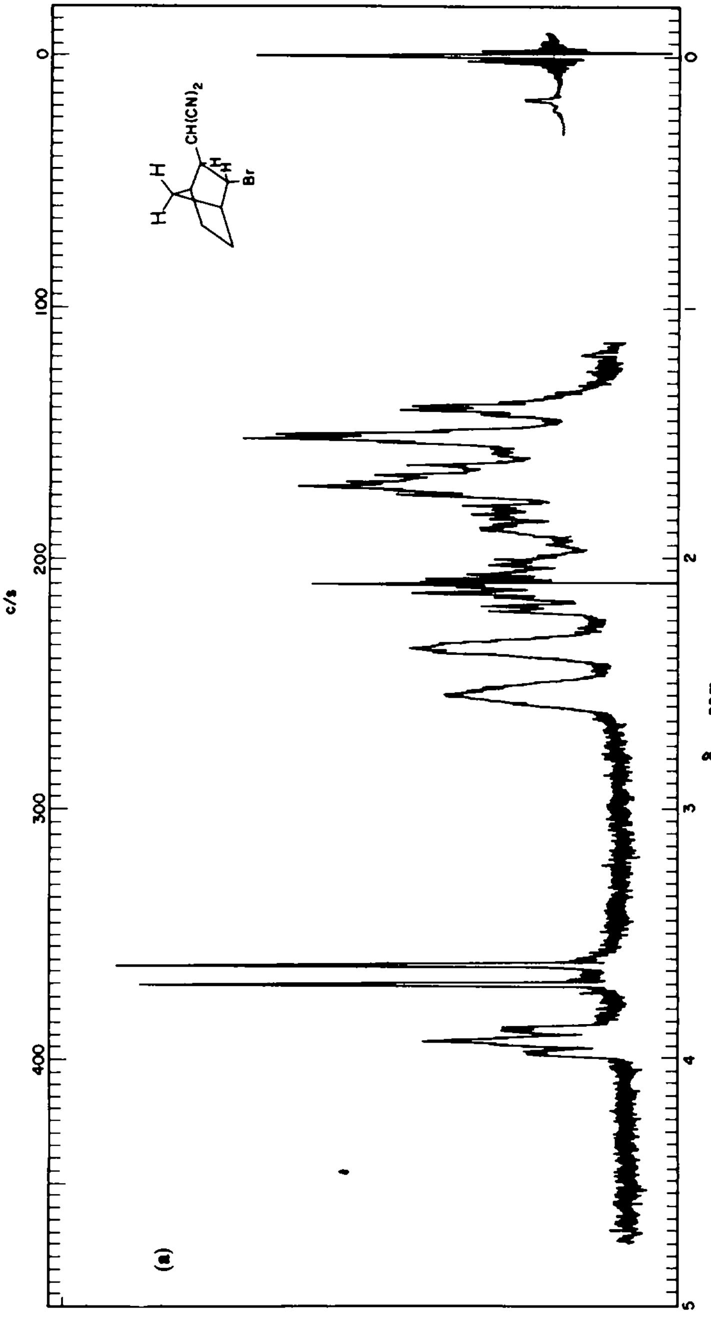


FIG 3. NMR spectrum (100 Mc) of the reaction product of bromodicyanomethane and *trans*-Δ^2-octalin (**1f**) treated with triethylamine (a) 400 mg in 1 ml tetrachloromethane (b) after shaking with deuteriumoxide plus a trace of triethylamine.

The three doublets at 3·76, 4·42 and 4·53 ppm are due to the weakly acidic protons of dicyanomethyl groups, since they disappear upon treatment with deuteriumoxide and a trace of triethylamine (Fig. 3b), as shown by the CH(CN)$_2$ NMR signal of *seqcis*-1-bromo-2-dicyanomethylcyclohexane (**3a**). By comparison with the spectrum of **3a** (Fig. 1), the doublet at 3·76 ppm (J = 10·5 c/s) and the broad band at 4·68 ppm may be assigned to the dicyanomethyl proton and the equatorial CHBr proton of **3f** (the corresponding bands of **3a** occur at 3·81 (J = 10·5 c/s) and 4·78 ppm). Similarly, comparison with the spectrum of **2a** (Fig. 1) leads to an assignment of the doublet at 4·53 ppm (J = 3·5 c/s) and of the multiplet at 3·9 ppm, which appears following deuteration (Fig. 3b), to the dicyanomethyl proton and the axial CHBr proton of **2f'**, respectively (**2a**; 4·55 (J = 3 c/s) and 3·95 ppm). The doublet at 4·42 ppm (J = 5·5 c/s) should then originate from the *cis* isomer **3f'**. The multiplet of the axial CHBr protons of **3f'** could lie at 3·8 ppm (Fig. 3b). By utilizing *p*-dichlorobenzene as internal standard, the total amount of isomers **2f'**, **3f** and **3f'** was spectroscopically (NMR) determined to be 6%, the individual contributions of the isomers being approximately equal. Therefore **2f** is formed to the extent of at least 94%.

Since in **2f'** the dicyanomethyl group and the Br atom are *trans* to each other, cyclization to **4f** (out of a twist-boat conformation of ring A) should be possible. Indeed, a 24 hr treatment with a large, 5-fold molar excess of triethylamine (with reference to bromodicyanomethane used for the addition reaction) leads to the disappearance of the band at 4·53 ppm, while the other peaks remain unchanged. Thus, the above structural assignment is substantiated. These observations also show that cyclization occurs much more rapidly if both substituents are *trans*-diaxial and ring A has a chair conformation.

It follows that *trans*-Δ^2-octalin (**1f**) is attacked by dicyanomethyl radicals with a high degree of selectivity from the directions marked by bold-faced arrows (equivalent to each other) with formation of an intermediate free radical with an axial dicyanomethyl group (**Rf**, Scheme 1). An intermediate free radical with an equatorial dicyanomethyl group can be formed in the case of octalin only if attack occurs from the directions marked by dotted arrows (again identical to each other) under primary formation of an intermediate radical **Rf'**, in which ring A has a twist-boat conformation.[6] This attack is therefore energetically unfavourable. In the following


c/s
0
100
200
300
400
δ, ppm
0
1
2
3
4
5
CH(CN)$_2$
H
H
H
H
Br
(a)

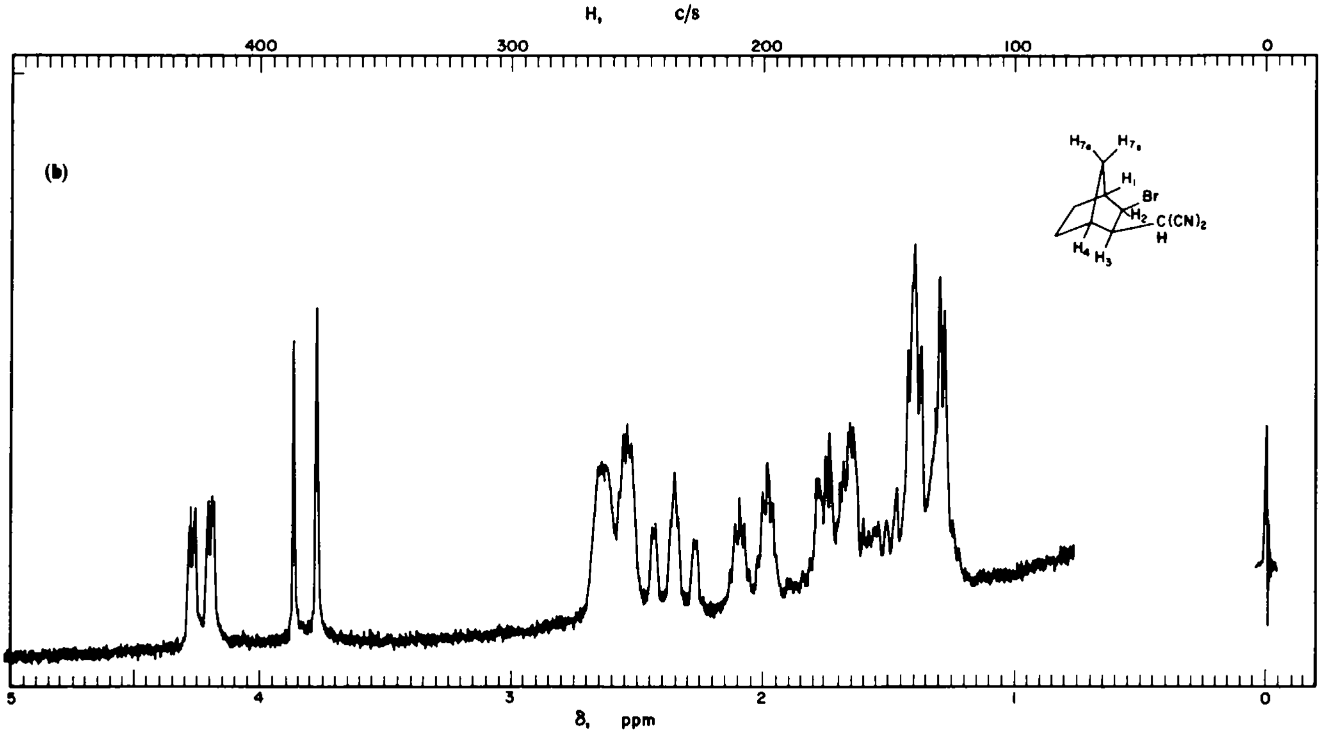
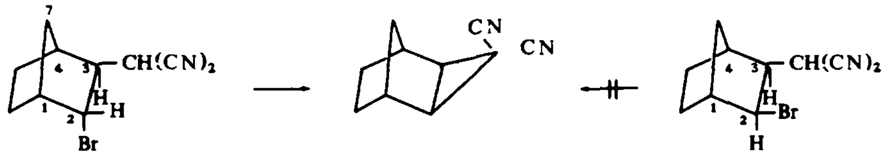


FIG 4. NMR spectrum (100 Mc) in CCl_4 (TMS internal standard) of (a) 2-*endo*-bromo-3-*exo*-dicyanomethylnorbornane (**2g**) and (b) 2-*exo*-bromo-3-*exo*-dicyanomethylnorbornane (**3g**).

discussion of the stereochemistry of the free radical addition of bromodicyanomethane, it is essential to keep in mind that attack by bromodicyanomethane on the intermediate radical product with an axial dicyanomethyl group (**Rf**) can again occur practically only from an axial direction with formation of **2f**.* The intermediate free radical product with an equatorial dicyanomethyl group (**Rf'**) must be attacked equally well from axial or equatorial directions since **2f'** and **3f** are formed in approximately equal amounts.

The addition of bromodicyanomethane to norbornene (**1g**) leads to isomers with dicyanomethyl groups in the *exo* position, 2-*endo*-bromo-3-*exo*-dicyanomethylnorbornane (**2g**) and 2-*exo*-bromo-3-*exo*-dicyanomethylnorbornane (**3g**), since bulky radicals always attack norbornene from the less hindered *exo* side.[11]



2g **4g** **3g**

The constitution of **2g** and **3g** is further derived from their NMR spectra (Figs 4a and b).†

Double resonance experiments with **2g** show that the CHBr proton at 3·95 ppm couples with the proton at C3 (centered at 2·17 ppm) to the extent of 3·9 ± 0·2 c/s. thereby proving that they are *trans* to each other, and with the bridge head proton (C1, broad peak at 2·57 ppm) with J = 5·3 ± 0·2 c/s. From this it follows that the C2 proton occupies the *exo* position and bromine thereby the *endo* position. In **3g**, the coupling constant of 7 ± 0·2 c/s between the CHBr proton at C2 (4 bands, centered at 4·25 ppm) and the C3 proton (3 bands, centered at 2·37 ppm) determined by means of double resonance points to a *cis* configuration, while the coupling constant between the bridge head proton at C1 (broad band at 2·65) and the proton at C2 (J = 0·5 ± 0·1 c/s) indicates *endo* configuration for the C2 proton and thereby *exo* configuration for bromine.

The cyclization of **2g** with triethylamine to 3,3-dicyanotricyclo[3.2.1.0^{2,4}]octane (**4g**) requires a much longer reaction time (up to 70 hr, 20°) than it does for **1a–f**. A model of **2g** shows that due to the rigid ring system a back-side attack of the dicyanomethyl anion on C2 is not easily accomplished. Moreover, the formation of the cyclopropane ring may be hindered by non-bonded interactions between the methylene bridge (C7) and a nitrile group.

MECHANISM

The free radical mechanism of the addition reaction of bromodicyanomethane to alkenes has been proved by inhibition experiments with oxygen and t.-butylcatechol.[2] Evidence for a chain reaction (reactions 3a and 3b) is provided by the marked acceleration of the reaction by relative weak irradiation. The actinometrically determined quantum yield for the photochemical initiation (253·7 nm, 30°) was shown to be 3·4 × 10^3 ± 10% for cyclopentene (**1d**) and 4·7 × 10^2 ± 10% for cyclohexene, (**1a**).

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* The *trans*/*cis* ratio given in Table 1 refers to **2f** and **3f'** present in the reaction mixture.

† The assignment of the bands and the steric conclusions based on the coupling constants follows from analysis of the NMR spectra of 2-*exo*- and 2-*endo*-chloro-3-*exo*-trichloromethyl-5,5-dimethylnorbornane.[13] We thank Dr. G. Schrumpf for carrying out the double resonance measurements of **2g** and **3g**.

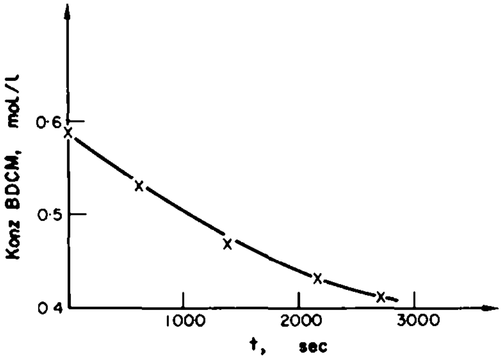

FIG 5. Photo-initiated reaction of bromodicyanomethane (0·588 Mol/l) with pentene (**1d**, 1·2 Mol/l) in methylene chloride (30°), effective flow of photons (253·7 mm) 2×10^{15}/sec.

As Fig 5 shows, the quantum yield remains approximately constant during the first one-third of the reaction. In the laboratory-scale addition experiments the quantum yield may well be higher, since the concentration of bromodicyanomethane is about 10 times as high and that of the alkene about 5 times as high.

Each light quantum absorbed must initiate two reaction chains. One corresponds to equations 1 and 3a, the other to addition of bromine radicals formed by 1 to an alkene with subsequent reaction according to 2b and 3a.* Therefore, the average chain length of the addition reaction of bromodicyanomethane (0·588 Mol/l) to **1d** is $1{\cdot}6 \times 10^3 \pm 10\%$ and to **1a** $2{\cdot}3 \times 10^2 \pm 10\%$, at alkene concentrations of ca. 1·2 Mol/l. These numbers represent a lower limit, since the calculation is based on the assumption that the quantum yield for the dissociation of bromodicyanomethane is $\phi_{diss} = 1$. If $\phi_{diss} < 1$, the true chain length would be greater. Moreover, the possibility of traces of oxygen in the reaction mixture cannot be ruled out with certainty.

Substitution reactions (4a, 4b), which are to be expected in a radical mechanism, occur only to a limited degree. For cyclohexene (**1a**), in which the allylic H atom apparently can be easily abstracted,[27] the value of the ratio $k_{addition}/k_{abstraction}$ with bromotrichloromethane is 1·2 (77·8°).[27] The high value of this ratio with bromodicyanomethane, 2500 (40°), must have its origin in the relatively high stability of the dicyanomethyl radical, which would also explain why reaction 3b is exothermic and very fast: With the exception of norbornene, which possesses unusual steric properties, none of the alkenes, although excess amounts of alkenes were always used, reacted to give telomers.

Slow addition of bromodicyanomethane may also be observed in the absence of light or other radical forming agents, e.g., **1d** reacts to give 5% conversion per hour. This, too, is a radical reaction, since it can be completely inhibited in the dark by addition of t-butylcatechol. Furthermore, the *trans*/*cis* ratio (**2a**/**3a**) for cyclohexene was identical to that measured in the light induced reaction (Table 2). It is conceivable that the radical reaction is initiated by a coupled reaction of bromodicyanomethane with the alkene (Eqs 2a and 2b), a mechanism similar to that proposed by Walling[28]

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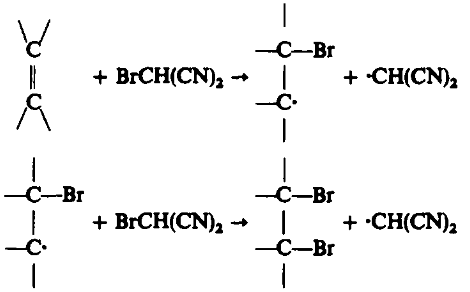
* Detection of slight amounts of 1,2-dibromocycloalkane in the reaction mixture does not prove this reaction sequence, since the dihalide may also be formed in a non-initiated radical reaction (see end of this page).

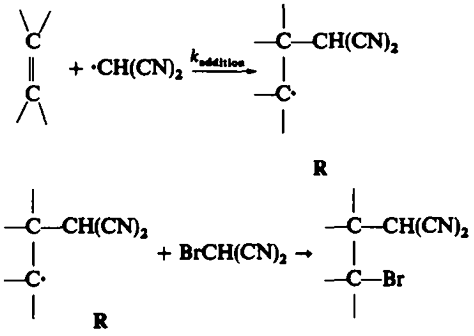
START

$$BrCH(CN)_2 \xrightarrow{h\nu} Br\cdot + \cdot CH(CN)_2 \qquad (1)$$


(2a)

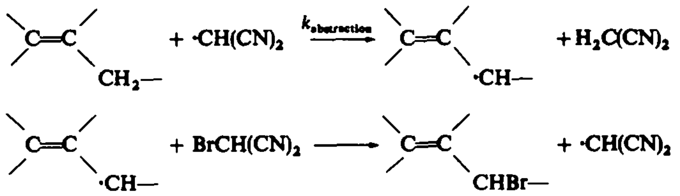
(2b)

CHAIN
addition


(3a)

(3b)

SUBSTITUTION


(4a)

(4b)

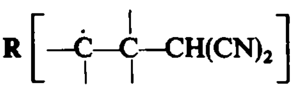
for the t-butylhypobromite addition. Indeed, up to 1% 1,2-dibromocyclopentan (with reference to bromodicyanomethane) could be identified by gas-chromatography in the non-induced addition reaction of bromodicyanomethane to cyclopentene.

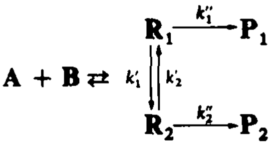
It should be noted, however, that the rate of the reaction in the dark depends upon the amount of water in the reaction mixture. If solvents and alkene are dried with molecular sieves, **1a**, for example, hardly reacts at all, and **1d** only at a rate of 2% conversion per hour. This indicates that a somewhat more complicated mechanism is operating.

DISCUSSION OF THE STEREOCHEMISTRY

Application of the Curtain–Hammett principle

As we were able to show, the relative energies of the transition states of reaction 3b, leading to the *trans* and *cis* products **2** and **3**, determine the *trans/cis* product ratio for each individual alkene. Thus, the Curtin–Hammett principle[29] is applicable to reaction 3b. This results in the first place from the fact that the reaction is kinetically and not thermodynamically controlled, i.e., under the employed conditions it is irreversible. Thus, for **1b**, **1c** and **1f** the thermodynamically less favorable products are formed. Furthermore, pure *trans* addition product, added to **1a** prior to start of the reaction, failed to take part in the reaction sequence as could be shown by quantitative gas chromatography of the reaction mixture.* Moreover, irradiation of **2b** in the presence of bromodicyanomethane failed to produce even a trace of **3b**.

The application of the Curtin–Hammett principle further demands that the free activation enthalpy for the conformational change of the intermediate free radical  $R\left[-\dot{C}-C-CH(CN)_2\right]$ is small compared to that of the follow-up reaction of **R** with bromodicyanomethane (reaction 3b). We were able to show that this is indeed the case: Reaction 3a corresponds to the general reaction scheme $A + B \rightleftharpoons R$ and reaction 3b may be represented by $R + XY \rightarrow P + X$. **R** may exist in two conformations, R_1 and R_2, which lead to products P_1 and P_2.† Thus we have the following reaction scheme:



The rates of the conformational conversions of R_1 and R_2 are then $k'_1[R_1]$ and $k'_2[R_2]$, respectively; those of the reactions of R_1 and R_2 to P_1 and P_2 are given by:

$$\frac{d[P_1]}{dt} = k''_1[R_1][XY]$$

and

$$\frac{d[P_2]}{dt} = k''_2[R_2][XY]$$

The ratio of the product forming rate to that of conversion of R_1 and R_2 is therefore $k''_1[XY]/k'_1$ and $k''_2[XY]/k'_2$, respectively. The smaller these ratios are, the better are the conditions for the application of the Curtin–Hammett principle. Small values arise if $k''/k' \ll 1$ or if $[XY]$ values are small.

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* Slow equilibration according to an ionic mechanism can also be excluded, since the *trans/cis* ratio does not change even upon longer standing of the reaction mixture.

† These lines of thought are of course also valid even if more than two forms of **R** are possible and for the case that more than one end product can form from **R**.

Since reduction of the concentration of bromodicyanomethane in the reaction of **1a** and **1b** by a factor of about 10^3, other conditions remaining constant, does not lead to a change in the *trans*/*cis* product ratio within the experimental error (Table 2), it is shown that the Curtin–Hammett principle is applicable.

Since reduction of bromodicyanomethane concentration by a factor of 100 in the reaction of *trans*-Δ^2-octalin also fails to cause a change in the product ratio (experimental uncertainty somewhat higher in this case), it is further clear that the backward reaction of 3a, i.e., the cleavage of a dicyanomethyl radical from **Rf** and **Rf'**, occurs much slower than reaction 3b. Otherwise the amount of endproducts with the energetically more favourable equatorial dicyanomethyl groups (**2f'**, **3f**, s. Scheme 1) would have increased. The reason for this behaviour may perhaps be due to the relative high ring strain in *trans*-Δ^2-octalin (**1f**)[30] which is relieved by addition of the dicyanomethyl radical.*

Using $P_{trans}/P_{cis} = e^{(G^{\ddagger}_{cis} - G^{\ddagger}_{trans})}/RT$,[29] we obtain for *trans*-Δ^2-octalin (**1f** $P_{trans}/P_{cis} \sim 27$) a $(G^{\ddagger}_{trans} - G^{\ddagger}_{cis})$ value of 2·1 kcal/mol. and for norbornene (**1g** $P_{trans}/P_{cis} = 0{\cdot}25$) a value of $-0{\cdot}8$ kcal/mol ($T = 313$°K).

In contrast to these two alkenes, for the cyclohexenes **1a–c** one must proceed on the assumption that more than one transition state leads to the *trans* and *cis* products (see below). Thus, $\Delta G_{trans-cis}$ values cannot be derived from the observed product ratios in these cases.

Structure of the transition states

ESR studies by Fessenden[31] and Ogawa[32] have shown that the cyclohexyl radical probably exists in the chair conformation and that the free radical C atom is sp^2-hybridized, i.e., its three bonds lie in a plane. By utilizing such a conformation for the cyclohexyl radical one can now explain, at least qualitatively, the observed *trans*/*cis* ratios. One condition for this treatment is that the degree of bond formation in the transition state is very small, i.e., the conformation of the free radical resembles that of the transition state. This assumption seems to be valid, since reaction 3b is fast and exothermic[33] (see page 3601).

For cyclohexene (**1a**) two intermediate free radicals with chair conformation and planar radical center are conceivable: **5A** and **5B** (R = H) (Scheme 2). As Jensen and Rodgers[34] were able to show, cyclohexyl radicals are attacked equally well from the "axial" and "equatorial" directions for the case of small development of the new bond in the transition state (Scheme 2). In the case discussed here the neighboring dicyanomethyl groups should have no effect on the direction of attack if it is in the equatorial position.† The two possible transition states derived from **5A** should be of approximately equal energy and the *seqtrans* (**2a**) and *seqcis* product (**3a**) ought to form in equal amounts. As is evident from the product ratio for octalin **1** , "equatorial" attack on **5B** (R = H) must be less favorable (by about 2 kcal/mol) than axial attack, i.e., 98% *seqtrans* product (**2a**) should be formed via **5B**. Since the free enthalpy of the transition state with conformation **5B** must be greater than that of the transition states derived from **5A** by an amount equal to the conformational energy of the dicyanomethyl group, it is understandable that the product ratio for cyclohexene (**1a**) in which the *seqtrans* product **2a** slightly dominates, is nearly statistical (**2a**/**3a** =

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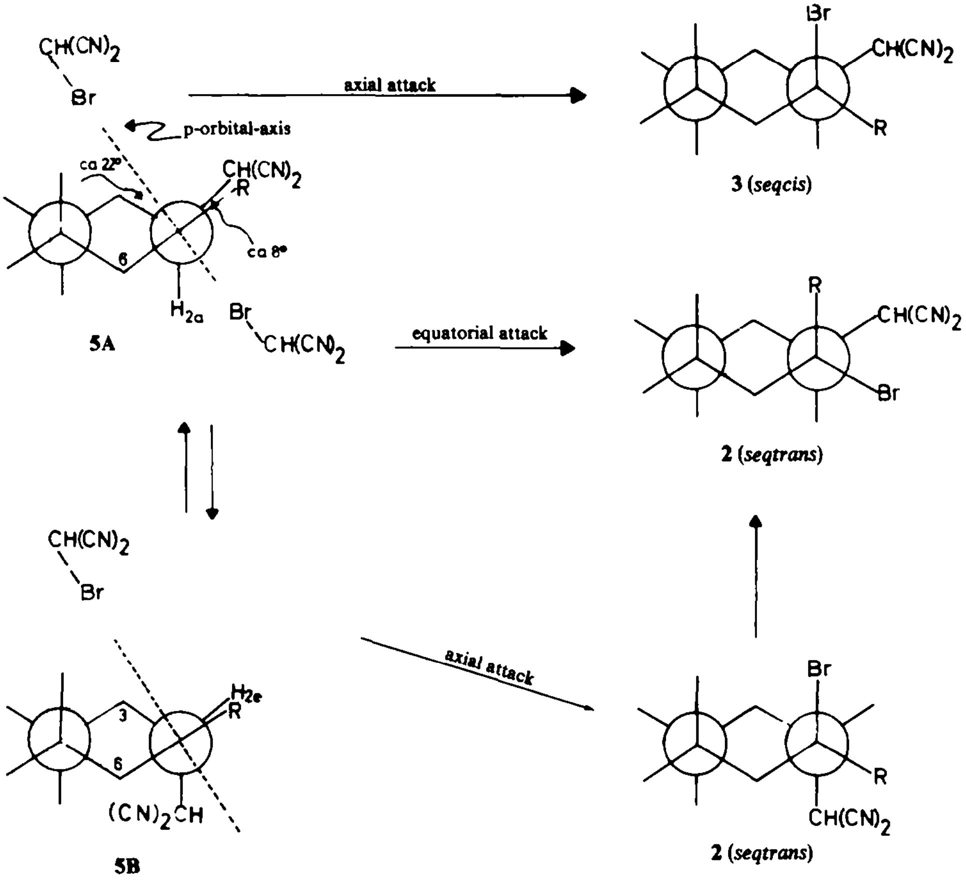
* Analogous circumstances prevail in the radical addition of thiols to **1** .[6] Whether the conformational equilibration of **R** in the case of cyclohexene or alkyl cyclohexenes occurs by ring inversion (which is impossible for **Rf** and **Rf'**) or by reversibility of reaction 3a, is irrelevant in the following discussion.

† If van der Waals repulsion forces between R(=H) and $CH(CN)_2$ in **5A** should be of significance, which is unlikely (rotational barrier ethane 2·8 and propane 3·2 kcal/mol), they should, just like torsional strain, become important only in case of more pronounced bond formation in the transition state and in that event operate in the same direction as torsional strain.

SCHEME 2*



* The bond angles shown in 5A and B are based on values determined by ESR measurements.[31]

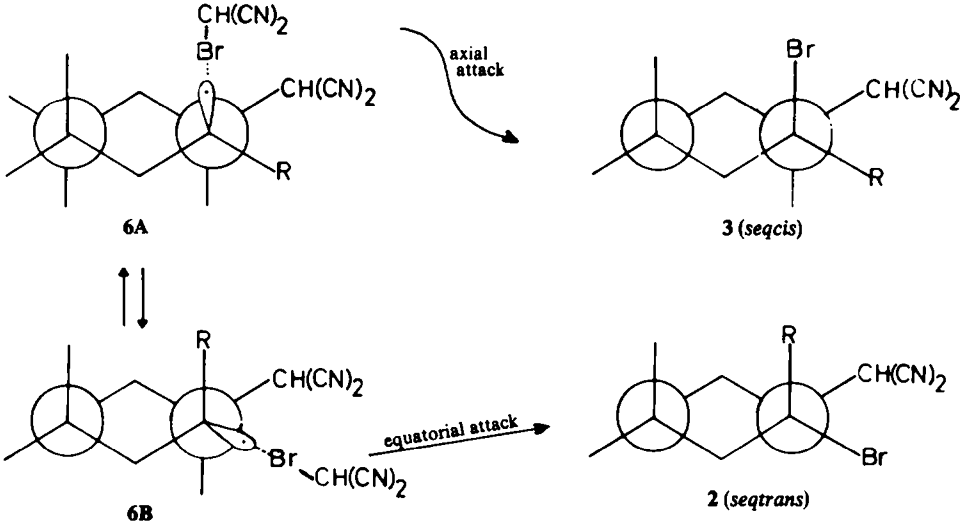
1·1). The exact values for **1a** are 52·3 ± 0·2% **2a** and 47·7 ± 0·2% **3a**. 4·6% *trans* product (**2a**) must have been formed by way of **5B** (R = H) and the remaining 95·4% isomeric mixture (of equal amounts of **2a** and **3a**) by way of **5A** (R = H). From these values a conformational energy of 1·7 ± 0·1 kcal/mol can be calculated for the dicyanomethyl group in the cyclohexyl radical (see Appendix).

Since with increasing temperature more products are formed via high energy transition states, the stereoselectivity of the addition reaction should increase with increasing reaction temperatures, i.e., the amount of *trans* product should increase. The experimental *trans*/*cis* ratio at 160° of 1·25 (55·5 ± 0·2% **2a** and 44·5 ± 0·2% **3a**) is reasonably consistent with the calculated conformational energy of the dicyanomethyl group (see Appendix) and lends support to the above lines of thought.

The high-temperature additions were carried out in *o*-dichlorobenzene instead of methylene chloride. However, the solvent dependence of the reaction is small. Addition of bromodicyanomethane to **1a** in benzene (30°) resulted in the same *trans*/*cis* ratio as in methylene chloride (Table 2).

As expected, the degree of allylic substitution increased somewhat at higher temperatures. The $k_{\text{addition}}/k_{\text{abstraction}}$ ratio at 160° is 16·5.

When R = H is replaced by a Me group, conformation 5A should become energetically less favorable as a result of van der Waals repulsion forces between R and the dicyanomethyl group (rotational barrier propane 3·2 kcal/mol and butane 4·4–6·2 kcal/mol), whereas conformation **5B** (R = Me) exhibits no such interactions. A greater participation of the conformation with axial dicyanomethyl group **5B** for R = Me should therefore be expected, leading to a greater amount of *trans* product. In this light the increasing *trans*/*cis* ratio going from cyclohexene (**1a**) to 1-methylcyclohexene (**1b**) is easily understood. The assumption of a planar free radical center in the transition state of reaction 3b for cyclohexene (**1a**) and 1-methylcyclohexene (**1b**) is further supported by consideration of the stereochemical consequences for the case that a tetrahedral and not a planar shape of the radical center corresponds to the structure of lowest energy.



6A

3 (*seqcis*)

6B

2 (*seqtrans*)

For cyclohexene (**1a**) essentially only the two conformations of lowest energy, **6A** and **6B** (R = H), should participate in the formation of the transition state. Thus, as the *trans*/*cis* ratio for **1a** (Table 1) shows, attack from axial and equatorial direction should be of equal energy.

Applying the assumption of a tetrahedral radical center to 1-methylcyclohexene (**1b**), one would expect that conformation **6A** (R = Me) is of lowest energy participating almost exclusively in the formation of the transition state. Correspondingly, almost only *cis*-product should be formed, which is not the case.

Since the tendency to form *cis* products in going from cyclohexene (**1a**) to 1-methylcyclohexene (**1b**) should also increase even if the radical C atom is not completely tetrahedral, it is thus shown, supplementary to and independently of the ESR measurements of the cyclohexyl radicals,[31, 32] that an sp^2-hybridization is the most favorable configuration of cyclohexyl and 1-methylcyclohexyl radicals. The conformational energy of an axial dicyanomethyl group of about 1·5 *kcal/mol thereby represents the approximate lower limiting value of the energy needed to force the radical out of its planar shape.*

Further increase in the size of the 1-alkyl group in cyclohexene should lead to increasing importance of van der Waals repulsion forces between R and H_{2e} as well as H_{6e} even in conformation **5B**. Since the energy difference between planar and tetrahedral radical conformation is probably small,[35] the steric strain could be largely relieved by transformation into conformation **6A** having a tetrahedral free radical center. More *seqcis* product should thus be formed with increasing bulkyness of R. Such a tendency can indeed be registered for 1-ethylcyclohexene (**1c**) and becomes even more obvious for 1-isopropylcyclohexene.[36] By determining the relevant conformational energies for these transition states, we arrive at a method for the determination of the *upper limiting energy values of the stability of a planar carbon atom radical.*

EXPERIMENTAL

Bromodicyanomethane. As described previously,[2] sufficiently pure bromodicyanomethane can be obtained only by the use of recrystallized (n-butanol) malonodinitrile. If commercial grade is used, the crude, dry bromodicyanomethane has to be purified with a little norite (chloroform) and recrystallized twice from chloroform (ca. −40°). Completely pure bromodicyanomethane remains colorless for months if water is excluded.

Addition reactions. The reaction of bromodicyanomethane with alkenes **1a–h** in CH_2Cl_2 (p.a., Merck) were carried out as described[2] under N_2 using a high pressure mercury vapor lamp (Q81–PL 327, Quarzlampengesellschaft Hanau) at a distance of ca. 20 cm. Following completion of the reaction, the mixture was usually colored slightly yellow; no bromodicyanomethane could be detected by means of a KJ/starch soln weakly acidified with AcOH. In the presence of O_2 or by the use of impure reagents, the reaction mixture turned brown to black, and not all of the bromodicyanomethane could be converted even upon prolonged irradiation. In these cases the bromodicyanomethane could be removed by washing with aqueous SO_2.

7,7-Dicyanonorcarane (**4a**). (a) The reaction mixture from bromodicyanomethane (14·5 g; 0·1 mol) and cyclohexene (10·2 g; 0·12 mol) in 30 ml CH_2Cl_2 (reaction time 7 hr, max temp 35°[a]) was treated with Et_3N (11 g; 0·11 mol) in 30 ml CH_2Cl_2, extracted with 2N HCl and water, finally shaken with 2N NaOH (1·3 hr), washed with water, then with saturated $NaHSO_3$aq and again with water. The conversion of **3a** into cyclohexanone and its separation was monitored gas chromatographically.[b] Upon evaporation, the residue crystallized extensively (on cooling to 0°); it was pressed on clay, affording **4a** (5·6 g; 38%) m.p. 53–59°. Double recrystallizations from light petroleum and cyclohexane followed by sublimation furnished pure **4a** m.p. 61–62°;[c] IR (KBr): —C≡N 2242 cm^{-1}; NMR[d]: two broad bands at 1·4 and 2·2 ppm. (Found: C, 73·80; H, 6·90; N, 19·10. $C_9H_{10}N_2$ (146·2) Requires: C, 73·94; H, 6·90; N, 19·16%). (b) The reaction mixture from bromodicyanomethane (12·4 g; 85 mmol) and cyclohexene (12·2 g; 0·15 mol) in 25 ml CH_2Cl_2 was treated with Et_3N (12·4 g; 0·12 mol) in 25 ml CH_2Cl_2. The product was washed with 2N HCl and water, the solvent removed and the residue distilled at ca. 1 torr. The fraction collected between 133–146° (bath temp up to 170°) was recrystallized from ligroin, furnishing **4a** (3·6 g; 29%) m.p. 56–57·5°.[c]

seqcis-1-*Bromo-2-dicyanomethylcyclohexane* (**3a**). The residue obtained after distilling off **4a** (method b) crystallized upon prolonged standing and yielded upon pressing on clay 4·5 g brownish crystals, **3a**, which, following recrystallization from ligroin, melted between 66 and 67·5° (3·8 g; 19%). Triple recrystallization from ligroin followed by high vacuum sublimation at 50–60° afforded pure **3a**, m.p. 68·0–68·5°;[c] IR (KBr): —C≡N 2237 cm^{-1}; NMR[d]: Broad band system 0·9–1·6 ppm (9). d. 3·84 (J = 10·2 c/s), broad band 4·72 (1). (Found: C, 47·74; H, 4·92; Br, 34·8; N, 12·42; Cl, 0·48.[e] $C_9H_{11}BrN_2$ (227·1) Requires: C, 47·60; H, 4·88; Br, 35·19; N, 12·33%).

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[a] In the experiments with cyclohexene, the reaction was irradiated at the start somewhat more strongly than in the case of open chain alkenes.

[b] Glass column with 2% Silicon Gum Rubber GE SE 30 on chromsorb W AW DMCS, Temp.-Program 70–150° 6°/min.

[c] Corrected, Berl-Block.

[d] In CCl_4, TMS internal standard, δ-values.

[e] The bromine used in the preparation of bromodicyanomethane contained some chlorine.

Reaction of **3a** *with alkali.* **3a** (110 mg) in 1·1 ml 5N NaOH were heated at 100° for 10 min. In the product after the distillation cyclohexanone was detected by means of gas chromatography. The m.p. and the mixed m.p. of the 2,4-dinitrophenylhydrazones (90 mg) were identical with cyclohexanone-2,4-dinitrophenylhydrazone.

Chromatographic separation of **2a** *and* **3a**. 150 mg of the crude reaction product from cyclohexene and bromodicyanomethane were chromatographed on a column (2·3 × 80 cm) filled with acidic silica gel[f] using CCl_4/benzene 6:5 as eluent. Complete separation could not be accomplished in this way. The fractions collected prior to the mixed fraction contained, however, as was shown[b] gas chromatography, pure **2a** (35 mg); the fractions which followed contained pure **3a** (20 mg).

seqtrans-1-*Bromo-2-dicyanomethylcyclohexane* (**2a**). The residue, obtained upon evaporation of the reaction product of bromodicyanomethane (22·8 g; 0·16 mol) and cyclohexene (16·4 g; 0·20 mol) in 50 ml CH_2Cl_2, was dissolved in 30 ml MeOH; the resulting soln was seeded with pure **2a** and kept at −40° for ca. 40 min while being vigorously stirred with a stream of N_2. The residue, filtered at −40°, was recrystallized 3 times from MeOH (−20 to −30°), dried, and collected to yield **2a** (4·8 g; 13%) m.p. 55·5–56·5°[c] Double recrystallization from light petroleum and sublimation in high vacuum yielded a product, m.p. 56·0–56·5°;[c] IR (KBr): $-C\equiv N$ 2235 cm^{-1}; NMR[d]: broad band system 1·1–2·9 ppm (9), broad, strongly split multiplet at 3·9 ppm (1), d 4·56 ppm (1, J = 3 c/s). (Found: C, 47·83; H, 5·01; Br, 35·38; N, 12·27; $C_9H_{11}BrN_2$ (227·11) Requires: C, 47·60; H, 4·88; Br, 35·19; N, 12·33%).

Addition of bromodicyanomethane to **1a** at 160°. Bromodicyanomethane (1·8 g) was added in one portion to **1a** (3 g) in 30 ml *o*-dichlorobenzene at 150° (bath temp 167°) and the mixture irradiated with exclusion of O_2. A few seconds later the temp in the mixture rose to 160–62° and then dropped off to 156°. After 15 min no bromodicyanomethane could be detected by means of KI/starch and the reaction was terminated. The **2a**/**3a** ratio in the original mixture was determined by gas chromatography (Table 2). 3-*Bromocyclohexene* was also determined by gas chromatography in the original product immediately following the termination of the reaction: 2m glass column with 2% neopentylglycol-sebacate on Chromosorb G, 100°, benzene as internal standard. The yield of 3-bromocyclohexene based on bromodicyanomethane was 5·7 ± 15%, compared to 0·04 ± 15% obtained from experiments carried out between 30 and 40°. The $k_{addition}/k_{abstraction}$ ratio is thus calculated to be 16·5 ± 15% at 160° and 2·5 × 10^3 ± 15% at 40°.

seqtrans-1-*Bromo*-1-*methyl*-2-*dicyanomethylcyclohexane* (**2b**). A soln of bromodicyanomethane (10·0 g; 69 mmol) and 8·0 g of **1b** (83 mmol) in 30 ml CH_2Cl_2 was irradiated 5 hr at 35–32°. Upon evaporation by standing in the air (3 days at ca. 10°), the mixture yielded **2b** in crystalline form. The crystals were centrifuged over Celite[g] and collected to give 11·2 g (m.p. 60–67°). Recrystallization from cyclohexane afforded 8·7 g colorless, pure **2b**, m.p. 76·5–78·0°.[c] The CH_2Cl_2 extracts from the celite were combined with the cyclohexane mother liquor, the solvents removed by evaporation, and the residue chromatographed on a column (2 × 30 cm) of acidic silica gel[f] using CCl_4/benzene (1:1) as eluent. The first fractions containing primarily **2b** next some **3b** were concentrated and recrystallized from cyclohexane yielding 0·7 g colourless crystals which were combined with the main fraction: 9·4 g (56%). Fourfold recrystallization from cyclohexane and high vacuum sublimation (50°) afforded **2b**, m.p. 78·5–79·0°;[d] IR (KBr): $-C\equiv N$ 2240 cm^{-1}; NMR[d] (100 Mc): broad band system 1·4–2·4 with a sharp s at 1·86, m 2·53 and d 4·53 (J = 1·6 c/s) ppm. Spin decoupling [saturation of the $CH(CN)_2$-proton, 4·53 ppm] showed that the m at 2·53 ppm corresponds to the C2 proton. (Found: C, 50·01; H, 5·43; Br, 33·05; N, 11·70. $C_{10}H_{13}BrN_2$ (241·1) Requires: C, 49·82; H, 5·44; Br, 33·12; N, 11·62%).

seqcis-1-*Bromo*-1-*methyl-2-dicyanomethylcyclohexane* **3b**. An additional amount of **3b** was obtained by washing the silica gel column used to separate **2b** (see above) with CCl_4/benzene (1:1). The residue upon concentration contained primarily **3b** (3·4 g) and, following recrystallization from cyclohexane/ligroin (1:1) plus a small amount of CCl_4 furnished 2·7 g colourless crystals, m.p. 51·5–52·5°[c] (16%), which were obtained in analytically pure form by triple recrystallization from low-boiling light petroleum and high vacuum sublimation at 45° (m.p. 52·5–53·0°);[c] IR (KBr): $-C\equiv N$ 2247 cm^{-1}; NMR:[d] broad band system 1·2–2·3 ppm with a sharp s at 1·96 ppm (together 12), d 4·10 ppm (1, J = 2·5 c/s). (Found: C, 49·7; H, 5·46; Br, 33·51; N, 11·4. $C_{10}H_{13}BrN_2$ (241·1) Requires: C, 49·81; H, 5·44; Br, 33·12; N, 11·52%).

1-*Methyl-7,7-dicyano-norcarane* (**4b**). A soln of 9·4 g of **2b** in 50 ml CH_2Cl_2 was stirred with 5 g Et_3N

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[f] After washing with 0·1 N HCl, activated at 120°.

[g] Celite 535: Kieselgur filter aid from Johns–Manville Co.

in 30 ml CH_2Cl_2 (ice cooling). After 5 min the mixture was treated with 100 ml 2N HCl while being cooled and stirred as previously, the organic phase washed with 100 ml 2N HCl and twice with water and dried (Na_2SO_4). The crystallized residue obtained upon evaporation was triturated with 30 ml light petroleum at 0°, yielding **4b** (5·9 g; 53% based on bromodicyanomethane; m.p. 33–36°). It was obtained analytically pure after triple recrystallization from light petroleum (b.p. 40°) and sublimation at 12 torr; m.p. 36·0–36·5°;[c] IR (KBr): —C≡N 2225 cm^{-1}; NMR[d]· broad band system 0·9–2·3 with a sharp s at 1·46 ppm. (Found: C, 74·84; H, 7·55; N, 17·49. $C_{10}H_{12}N_2$ (160·2) Requires: C, 74·96; H, 7·55; N, 17·49%).

seqtrans-1-*Bromo-1-ethyl-2-dicyanomethylcyclohexane* (**2c**). The reaction mixture[b] from the 7 hr irradiation of bromodicyanomethane (11·6 g; 0·08 mol) and 11 g of **1c** (0·1 mol) in 60 ml CH_2Cl_2 was recrystallized according to the method employed for **2a** from 50 ml MeOH at −50° (2 hr) furnishing 2 g of **2c**. Additional 6 g were obtained by applying the same procedure to the filtrate which had been concentrated to 25 ml. Recrystallization from 20 ml cyclohexane gave 5·3 g (20%) **2c**, which melted at 71°[c] following high vacuum sublimation (65°); IR (KBr): —C≡N 2230 cm^{-1}; NMR (100 Mc)[d]: t 1·07 (J = 7 c/s), broad multiplet 1·2–3·3 and 2·4–2·8 (3), d 4·63 ppm (1, J = 1·7 c/s). Spin decoupling (irradiation at 4·63 ppm) showed that the signal of the C2 proton appears as a multiplet centered at 2·68 ppm; it is thus predominantly equatorial (the signal of the C3 proton in **2f** appears at 2·77 ppm). The energetically most favourable conformation of **2c** thus has an axial dicyanomethyl-group, an axial bromine and an equatorial ethyl group. (Found: C, 51·84; H, 5·86; Br, 31·54; N, 10·82. $C_{11}H_{15}BrN_2$ (255·2) Requires: C, 51·78; H, 5·92; Br, 31·32; N, 10·98%).

seqcis-1-*Bromo-1-ethyl-2-dicyanomethylcyclohexane* (**3c**). The residue obtained upon concentration of the mother liquors in the isolation of **2c** was recrystallized from cyclohexane/light petroleum (1:1), yielding **3c** (1·5 g; 7%), which after high vacuum sublimation (65°) melted at 73°;[c] IR (KBr): —C≡N 2240 cm^{-1}; NMR[d]: CH_3 t 1·11 (3, J = 7 c/s), m 1·3–2·5, d 4·18 (1, J = 2·5 c/s) ppm. (Found: C, 51·89; H, 5·85; Br, 31·41; N, 10·91. $C_{11}H_{15}BrN_2$ (255·2) Requires: C, 51·78; H, 5·92; Br, 31·32; N, 10·98%).

1-*Ethyl-7,7-dicyanonorcarane* (**4c**). **2c** (1·6 g) yielded upon cyclization (in order to obtain complete conversion, the mixture has to be stirred for 20 min at 0°) and isolation, as described for **4b**, 0·8 g **4c** (73%) in the form of a colourless liquid. It was obtained analytically pure by distillation at 117° (1·5 torr), n_D^{20} 1·4892; IR (film): —C≡N 2230 cm^{-1}; NMR[d]: band system 0·9–2·2 ppm. (Found: C, 75·40; H, 8·15; N, 16·19. $C_{11}H_{14}N_2$ (174·3) Requires: C, 75·82; H, 8·10; N, 16·08%).

seqtrans-1-*Bromo-dicyanomethylcyclopentane* (**2d**). The reaction mixture from bromodicyanomethane (14·5 g; 0·1 mol) and **1d** (9·0 g; 0·13 mol) in 20 ml CH_2Cl_2 (irradiation time 5 hr) was concentrated and dissolved in 30 ml MeOH. The product (enriched in **2d**), which crystallized between −20° and −30°, was recrystallized 3 times from MeOH at −20° to −40°, dried and sublimated at ca. 0·5 torr (cold finger at −40°), yielding 6 g (28%) **2d**, m.p. 21·0–21·5°;[c] NMR:[d] broad band system 1·5–3·0 (7), d 4·10 ppm (J = 4 c/s) overlapping with broadly split multiplet (together 2). (Found: C, 45·18; H, 4·32; Br, 37·30; N, 13·02. $C_8H_9N_2$ (213·1) Requires: C, 45·10; H, 4·26; Br, 37·50; N, 13·15%).

6,6-*Dicyano-bicyclo*[3.1.0]*hexane* (**4d**). The 5 hr reaction of bromodicyanomethane (22·1 g; 0·15 mol) with **1d** (13·2 g; 0·19 mol) in 50 ml CH_2Cl_2 followed by treatment with Et_3N (18 g; 0·18 mol) in 30 ml CH_2Cl_2 was worked up as in **4a** (method b). The fractions between 93 and 105° (ca 1 torr) were cooled, pressed on clay, recrystallized and again pressed on clay, yielding **4d** (10·4 g; 51%), m.p. 31·5–33·5°. After recrystallization from a little MeOH and light petroleum (3 times) and sublimation (16 torr) m.p. 34·0–35·0[c] IR (KBr): —C≡N 2220 cm^{-1}; NMR[d]: broad band system 1·3–2·7 ppm. (Found: C, 72·80; H, 6·30; N, 21·20. $C_8H_8N_2$ (132·2) Requires: C, 72·70; H, 6·10; N, 21·20%).

seqcis-2-*Bromo-1-dicyanomethyl-cyclopentane* (**3d**). The distillation residue from **4d** was filtered through a column (3 × 60 cm) of neutral silica gel (CCl_4/benzene 4:1). The eluent was concentrated, and the residue pressed on clay, affording 2·0 g (6%) colourless crystals, which after recrystallization and sublimation (1 torr, 50°) melted at 48·5–49·5°;[c] IR (KBr): —C≡N 2247 cm^{-1}; NMR[d]: broad band system 1·4–2·9 (7), d 3·81 (1, J = 10·5 c/s), broad s 4·65 (1) ppm. (Found: C, 44·95; H, 4·16; Br, 37·45; N, 13·06. $C_8H_9BrN_2$ (213·1) Requires: C, 45·09; H, 4·26; Br, 37·50; N, 13·15%).

seqtrans-1-*Bromo-1-methyl-2-dicyanomethylcyclopentane* (**2e**). A mixture of bromodicyanomethane (21·1 g; 0·15 mol) and **1e** (14·0 g; 0·17 mol) in 35 ml CH_2Cl_2 was treated with 35 ml light petroleum following

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[b] This reaction was carried out together with J. Oberdörfer.

irradiation (4 hr, max, temp. 38°). After 3 hr at − 60°, practically pure **2e** (12·6 g; 38%) precipitated. After double recrystallization from MeOH (at − 30 to − 40°) and light petroleum and drying, they melted at 39·0–40·0° and were obtained analytically pure by drying (25°, high vacuum). On prolonged standing, **2e** decomposes (20°); IR (KBr): —C≡N 2250 cm^{-1}. (Found: Br, 35·15; N, 12·28. $C_9H_{11}BrN_2$ (227·1) Requires: Br, 35·19; N, 12·33%).

seqcis-1-*Bromo-methyl-2-dicyanomethylcyclopentane* (**3e**). The MeOH from the mother liquor of **2e** was removed by distributing between water and CH_2Cl_2. The soln was concentrated (rotary evaporator with cooler at − 30°), and the residue, dissolved in 12 ml MeOH, seeded at − 30 with **2e**. The crystalline product (primarily **2e**) was suction filtered and again recrystallized in the same manner. The mother liquors were combined and separated from MeOH as described above. By repeated crystallization of the residue obtained in this way from 10 ml MeOH at − 30 to − 40°, **3e** was accumulated in the solid product.

After removal of the seeding agent (kept at − 30°), the material (in 30 ml CH_2Cl_2) was treated with a soln of 4 ml Et_3N in 20 ml CH_2Cl_2 at 0°; the mixture was stirred for 5 min, extracted twice with 2 N HCl, washed with water, dried (Na_2SO_4) and concentrated (vacuum, 20–25°). The residue (kept in 12 ml MeOH for 30 min at − 30°, seeded with a sample obtained earlier) furnished a solid material which was recrystallized from MeOH (10 ml, − 30°, 1 hr), yielding 1·3 g of pure **3e**. Additional **3e** was obtained by combining the mother liquors from the three crystallizations and cooling to − 50 to − 60°, which was purified by recrystallization from MeOH at − 30°, total yield 1·8 g (5·5%). The material was obtained analytically pure by additional recrystallizations from MeOH (− 30°) and pentane, m.p. 44·0–44·5°[c]; IR (KBr): —C≡N 2232 cm^{-1}. (Found: C, 47·48; H, 5·01; Br, 34·0; N, 12·35; Cl, 0·75.[e] $C_9H_{11}BrN_2$ (227·1) Requires: C, 47·60; H, 4·88; Br, 35·19; N, 12·33%).

1-*Methyl-6,6-dicyano*[3.1.0]*hexane* (**4e**). The reaction mixture from *bromodicyanomethane* (14·5 g; 0·1 mol) and **1e** (10·1 g; 0·12 mol) in 35 ml CH_2Cl_2 was concentrated at 25° (vacuum, rotary evaporator, cooler − 30°). The residue was recrystallized twice from MeOH (− 30 to − 40°), yielding practically pure **2e** (12 g). This was cyclized as in **4a** (method b) with Et_3N (8 g in 40 ml CH_2Cl_2), furnishing after double recrystallization from MeOH (− 30 to − 40°) and distillation (80°–90°, ca. 1 torr) pure **4e** (54 g; 37%) m.p. 28·5–29·5°; IR (KBr): —C≡N 2222 cm^{-1}; NMR:[d] broad band system 1·4–2·4 with a sharp s at 1·54 ppm. (Found: C, 73·82; H, 7·05; N, 19·01. $C_9H_{10}N_2$ (146·2) Requires: C, 73·94; H, 6·90; N, 19·16%).

2α-*Bromo*-3β-*dicyanomethyl*-trans-*decalin* (**2f**). The reaction mixture from bromodicyanomethane (7·27 g; 50 mmol) and **1f**[f] (8·7 g; 64 mmol) in 30 ml CH_2Cl_2 (10 hr irradiation time) was concentrated. The crude product was centrifuged over celite and recrystallized from CCl_4, affording 12·5 g (90%) **2f**, m.p. 119°; IR(KBr): —C≡N 2245 cm^{-1}; NMR see Fig. 2. The chemical shift of the dicyanomethyl proton depends to a high degree upon the solvent (d_6-acetone 4·85, CCl_4 3·80 and d_6-benzene 2·70 ppm). The same effect was observed for in malodinitrile.[38] (Found: C, 55·69; H, 5·98; Br, 28·22; N, 10·03 $C_{13}H_{17}BrN_2$ (281·2) Requires: C, 55·53; H, 6·12; Br, 28·42; N, 9·93%).

4,4-*Dicyano-tricyclo*[5.4.0^{trans}.0^{3,5}]*undecane* (**4f**). **2f** (3 g; 1·07 mmol) in 30 ml CH_2Cl_2 was treated with 6 g Et_3N (ice cooling), and the mixture stirred for 5 min, washed twice with 2 N HCl and water, and dried. The concentrated residue was recrystallized from light petroleum, yielding **4f** (20·4 g; 90%), m.p. 73°.[c] Sublimation at 70°, 1 torr furnished analytically pure **4f**; IR (KBr): —C≡N 2230 cm^{-1}; NMR:[d] broad band system 0·6–2·7 ppm. (Found: C, 77·88; H, 8·20; N, 14·09. $C_{13}H_{16}N_2$ (200·3) Requires: C, 77·96; H, 8·05; N, 13·99%).

2-exo-*Bromo*-3-exo-*dicyanomethyl-norbornane* (**3g**). The concentrated residue of the reaction of bromodicyanomethane (25 g; 0·17 mol) and **1g** (18·8 g; 0·2 mol) in 40 ml CH_2Cl_2 (irradiation time 5 hr) yielded upon fourfold recrystallization from MeOH (− 40°) and recrystallization from ligroin/CCl_4 (1 :1) pure **3g** (5 g; 12%) m.p. 48–49°.[c] This was obtained analytically pure by sublimation at 70°, 1 torr; IR (KBr): —C≡N 2237 cm^{-1}; NMR spectrum see Fig. 4b. (Found: C, 50·40; H, 4·79; Br, 33·30; N, 11·70. $C_{10}H_{11}BrN_2$ (239·1) Requires: C, 50·23; H, 4·64; Br, 33·42; N, 11·72%).

When a 1·4 molar excess of **1g** was used, a white, amorphous ppt formed upon addition of MeOH to the oily concentrated residue. Its behavior at the m.p. (190–200° decomposition) and the non-characteristic NMR spectrum points to a norbornene-polymer; IR (KBr): weak —C≡N band at 2240 cm^{-1}.

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[f] **1f** was separated gas chromatographically (6 m columns with Carbowax 20 M on Kieselgur 0·3–0·4 mm, 170°) from the *cis–trans*-Δ^2-octalin mixture, accessible according to the procedure of Johnson.[37]

2-endo-*Bromo*-3-exo-dicyanomethylnorbornane (**2g**). The concentrated residue from the mother liquors of **3g** was recrystallized from a little MeOH 6 times (− 40°) and sublimed (16 torr' 110°): **2g** (0·8 g; 2%) m.p. 74·0–74·5°; IR (KBr): —C≡N 2242 cm^{-1}; NMR spectrum see Fig. 4a. (Found: C, 50·20; H, 4·79; Br, 33·45; N, 11·60. $C_{10}H_{11}BrN_2$ (239·1) Requires: C, 50·23; H, 4·64; Br, 33·42; N, 11·72%).

In the described separation of **2g** and **3g**, a great deal of substance is lost and only small amounts of pure isomers are obtained. The total yield of **2g** and **3g**, as determined by gas chromatography (silicone gum GE SE 30 on Haloport F, 135°, 9,10-dihydroanthracene as standard), was 95–98% based on bromodicyanomethane.

3,3-*Dicyano-tricyclo*[3.2.1.0$^{2.4}$]*octane* (**4g**). The crude product obtained from the reaction of bromodicyanomethane (25 g; 0·17 mol) and **1g** (18·8 g; 0·2 mol) in 40 ml CH_2Cl_2 (irradiation time 5 hr) was treated with Et_3N (19·2 g; 0·19 mol) in 25 ml CH_2Cl_2 and stirred for 70 hr at 20°. The concentrated residue was washed with 2 N HCl and water, and the dried red-brownish soln filtered over acidic silica gel^{f} (benzene/CCl_4) and distilled (ca. 3 torr, b.p. 70°). The crystals which deposited on the cooler (m.p. ca 78°) were recrystallized three times from cyclohexane and sublimated at 100° (16 torr), yielding 1·3 g (5%) **4g** m.p. 85·5–86·5°^{c} IR (KBr): —C≡N 2222 cm^{-1}; NMR:^{d} m 0·8–2·1, broad s 2·8 ppm. (Found: C, 75·84; H, 6·48; N, 17·66; $C_{10}H_{10}N_2$ (158·2) Requires: C, 75·92; H, 6·37; N, 17·71%).

6,6-*Dicyano*-2,3-*benzo*-bicyclo[3.1.0]*hexene*-(2) (**4h**). The product from the reaction of bromodicyanomethane (7·27 g; 50 mmol) and **1h** (7·8 g; 64 mmol) in 30 ml CH_2Cl_2 (irradiation time 1 hr, max temp 30°) was chromatographed on a column (3·5 × 100 cm) of neutral silica gel (chloroform). Green and brown zones developed at the head of the column; the contents of the eluent yielded upon several recrystallizations from CCl_4 **4h** (0·9 g) of m.p. 96·5°;^{c} IR (KBr): —C≡N 2230 cm^{-1}; NMR (in d_6-acetone, TMS internal standard): m 3·1–3·55 (3), d 3·93 (1, $J = 6$ c/s), m 7·2–7·7 (4) ppm. (Found: C, 79·89; H, 4·52; N, 15·42. $C_{12}H_8N_2$ (180·2) Requires: C, 79·78; H, 4·48; N, 15·55%).

Determination of the trans/cis *ratios*

The *trans/cis* ratio for **1a** was determined by gas chromatography using the original reaction mixture: 2 m glass column with 2% silicone rubber GE SE 30 on Chromosorb W AW DMCS, column temp 130–140°, flame ionization detector. It was demonstrated that the ratio of the peak areas of both isomers are equal to the mole ratios: Test mixture of **2a**/**3a** = 1·078, peak ratio found 1·074 (average of 10 measurements). Average uncertainty ± 0·004. The peak areas were determined by weighing. The values given for every experiment are the average of 5 chromatographic determinations.

The addition products of bromodicyanomethane to **1b**, particularly **2b**, are somewhat less stable than those of **1a**. In the gas chromatographic determination (column as in **1a**, temp of column *and* injection port 140°) of *trans*/cis ratios, the peak areas were calibrated with a mixture of **2b** and **3b** (containing 69·3% **2b**), whereby the calibration chromatograms were recorded between the sample solutions. The calibration factor k was found to be 1·063 (F: peak area in the gas chromatogram).

$$k = \frac{\text{sample weight}_{seqtrans} \times F_{seqcis}}{\text{sample weight}_{seqcis} \times F_{seqtrans}}$$

The instability of **2c** and **2e** is so pronounced, that even upon calibration no direct gas chromatographic analysis of the *trans/cis* ratio could be carried out. Consequently, in case of **2e**, a sample of the reaction mixture (1ml) was treated with 0·5 g Et_3N in 2 ml CH_2Cl_2; after filtering off the Et_3NHBr, the soln was washed with 2 N HCl and a little water, and dried over Na_2SO_4. The ratio **4e**/**3e** was then determined. The peak areas were calibrated with standard measurements using pure **4e**. The composition of the product mixtures from **1c** and from the dilution experiment with **1b** was determined NMR spectroscopically using the intensity of the dicyanomethyl proton of **2c** and **3c**, and **2b** and **3b**. The uncertainty was approximated at ± 5%.

The mole fractions of the *seqtrans* product determined in this manner are given in Table 2, which also contains additional information concerning the method of determination.

Light measurements. The light measurements in the determination of the quantum yield of the addition reaction $\phi = P/x$ (P = number of molecules of product, x = number of light quanta absorbed in the reaction) were carried out with the aid of an experimental setup shown in Fig 6.

A low-pressure mercury lamp (Firma Gräntzel, Karlsruhe, 200 mA/500 V) served as the light source. In the preceding case the lamp furnished practically monochromatic light of 253·7 nm, since the above quartz apparatus absorbed the line at 184·9 nm, while the weak emission at 577–579 nm[39a] is not absorbed by the reaction mixture (concerning the extinctions of bromodicyanomethane, see loc. cit.[2]). The low-

TABLE 2. ISOMER RATIOS FOR THE REACTION OF BROMODICYANOMETHANE WITH CYCLOALKENES

	Alkene,[a] g	Bromo-dicyane-methane, g	Solvent, ml	Irradiation time, hrs.	Maximum reaction Temperature	Seqtrans-product mole-fraction
1a	5·0	7·25	CH_2Cl_2, 15	4	42°	0·523 ± 0·002
	2·0	0·091	CH_2Cl_2, 70	4	36°	0·519 ± 0·002
	3·0	3·0	CH_2Cl_2, 5	16 (reaction in in the dark)	25°	0·51
	3·0	1·8	o-Dichlorbenzol, 30	0·25	161°	0·555 ± 0·002
	7·0	6·6	C_6H_6, 20	9	35°	0·53
1b	6	5	CH_2Cl_2, 10	7	37°	0·687 ± 0·005[b]
	2	0·105	CH_2Cl_2, 60	1	36°	0·68 ± 0·03[c,d]
1c	11	11·6	CH_2Cl_2, 60	7	38°	0·61 ± 0·03[c,d]
1d	10	14·5	CH_2Cl_2, 10	5	38°	0·79[d]
	2[e]	0·0905	CH_2Cl_2, 70	5	35° (const.)	0·78[f]
1e	5	5	CH_2Cl_2, 20	4	38°	0·72[g]
1g	18·8	25	CH_2Cl_2, 40	5	37°	0·22[h]

[a] Quantity used for distillation; [b] Average value of 4 addition experiments, each with 3 to 4 measurements; [c] NMR-spectroscopically determined, see page 3611; [d] Determined by gas-chromatography; 2 meter glass column 2% Silicone Rubber GE SE 30 on Chromosorb W AW b MCS, 130°, injection port 135°; average value of three experiments; maximum deviation 0·01; [e] After distillation of methylene-chloride injected into the reaction mixture; [f] Determined by gas-chromatography; 3 meter glass column, diameter 4 mm, 1·5% Silicone Rubber GE SE 30 on PTFE (Haloport F, from F & M Scientific) temp 110°, injection port 135°; [g] Determined by gaschromatography; column as for [f]. Temperature 130°; average value of four experiments; Maximum deviation 0·01. [h] Determined by gas chromatography. Column as for [f], temp. 135°.

pressure lamp was thermostatically controlled due to the temperature dependence of the radiation intensity.[39b] The size and inter-distance of the disc diaphragms and the inter-distance between the quartz lense and the light source were chosen so as to insure that a nearly parallel light beam reaches the cells.

For the light measurement 0·006 M ferric-potassium-oxalate in 0·1 N H_2SO_4 was used in cell II (according to Hatchard and Parker[39c, 40]). In the determination of the photochemically formed ferrous ions, 2 ml were withdrawn from cell II, treated with 2 ml of 0·1% aqueous 1,10-phenanthroline and 5 ml buffer soln (60 ml 1 N CH_3COONa, 360 ml 1 N H_2SO_4 filled with water to yield 1 l) and filled up to 25 ml with 0·1 N H_2SO_4. After 1 hr the soln was photometrically analyzed (510 nm) (Zeiss-Spectralphotometer, RPQ 20 AV; the molar extinction of the Fe^{++}-phenanthroline complex at 510 nm was determined to be $\varepsilon = 1{\cdot}13 \times 10^4$, lit.[39c]: $1{\cdot}11 \times 10^4$).

In the determination of the quantum flow of the light source, cell I was filled with cyclohexene (1·2 M) in CH_2Cl_2 (p.a., Merck, dried with molecular sieves 5 Å). At a lamp temp of 30° (35°), it had a value of 1·75 (7·95) × 10^{15} ± 5% quanta/sec. The relative high average error may be due to variation in the emission of the low-pressure lamp. When a high-pressure mercury lamp was used in a similar experimental setup, the reproducibility was better than ±2%.[41] Since the number of light quanta absorbed in the reaction x is determined by the difference between two light measurements, x and thereby ϕ have an uncertainty of ± 10%.

Determination of the quantum yield. About 3·5 g (0·05 mol) of **1d** or 4·1 g (0·05 mol) **1a** in 80 ml CH_2Cl_2 (p.a., Merck, previously dried over molecular sieves 5 Å) were distilled in very weak red light (under an atmosphere of dry N_2) to 3·6 g (0·025 mol) dry bromodicyanomethane in cell I, which had been previously

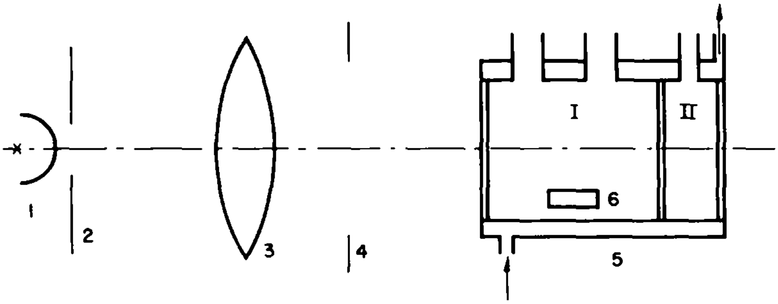

FIG. 6 Setup for determining quantum yields.
(1) mercury low-pressure lamp controlled thermostatically (30° and 35°, respectively); (2) disc diaphragm; (3) quartz lense; (4) disc diaphragm; (5) thermostatically controlled cell with quartz window, diameter 5 cm, I for reaction mixture, length 4 cm; cell II for actinometer-solution, length 1 cm; (6) stirrer.

flushed with dry N_2 for 4 hr, irradiated (with stirring at 30° with a quantum flow of $7{\cdot}95 \times 10^{15} \pm 5\%$ quanta/sec for 10 min (lamp temp 35°) and determined the amount of reacted bromodicyanomethane iodometrically: 0·5 ml of the reaction mixture was treated with 10 ml acetone, 5 ml 0·5 N KI, 17 ml water and 3 ml AcOH; the mixture was titrated with 0·1 N $Na_2S_2O_3$.

Cyclopentene: 28% conversion of bromodicyanomethane quantum yield $3{\cdot}4 \times 10^3 \pm 10\%$
Cyclohexene: 10% conversion of bromodicyanomethane quantum yield $4{\cdot}7 \times 10^2 \pm 10\%$.

Parallel experiments without irradiation showed that if moisture is excluded (use of carefully dried bromodicyanomethane and drying cyclohexene and CH_2Cl_2 with molecular sieves), no measurable reaction in the dark took place with cyclohexene. The 2% measured for cyclopentene was neglected in the calculation of the quantum yield.

Proof of the irreversibility of the addition to **1a**. After 10 hr of irradiation of a mixture of bromodicyanomethane (1·45 g; 30 mmol), **1a** (2·5 g; 30 mmol) and **2a** (0·65 g; 0·65 mmol) in 15 ml CH_2Cl_2 (p.a.), no bromodicyanomethane could be detected (KI/starch). The soln was concentrated to ca. 5 ml and analyzed gas chromatographically as described on page 3611. Mole fraction **2a** Calc:* 0·635; Found: 0·634.

Proof of the irreversibility of the addition to **1b**. A mixture of bromodicyanomethane (0·4 g) and **2b** (0·5 g) in 20 ml CH_2Cl_2 were irradiated for 3 hr under an atmosphere of N_2. In the reaction mixture **3b** could not be determined (neither NMR spectroscopically nor gas chromatographically, 4m glass column, 1·5% silicon gum on Haloport F, 150°).

APPENDIX

Calculation of the conformational energy of the 2-dicyano-methyl group in the cyclohexyl radical (see page 3605)

The following simplifying assumptions were made: (a) For the two transition states derived from conformation 5A (R = H), $\Delta G^{\ddagger}_{A\,trans} = \Delta G^{\ddagger}_{A\,cis}$ (b) The energy of the transition state derived from conformation **5B** (R = H) ($\Delta G^{\ddagger}_{B}$) differs from $\Delta G^{\ddagger}_{A\,trans}$ only by the conformational energy of the axial dicyanomethyl group (ΔG_{DCM}). (c) $\Delta G^{\ddagger}_{A\,trans} - \Delta G^{\ddagger}_{B\,trans} = \Delta G_{5A} - \Delta G_{5B} = \Delta G_{DCM}$.

Utilizing the ratio 47·7/4·6 (**2a** formed via 5A/**2a** formed via **5B**), we obtain for 160° $\Delta G^{160^\circ}_{DCM} = 1{\cdot}2 \pm 0{\cdot}1$ kcal/mol. and for $\Delta G^{40^\circ}_{DCM} = 1{\cdot}4 \pm 0{\cdot}1$ kcal/mol. The values just barely lie within the experimental uncertainty in the determination of **2a** and **3a**. ΔG_{DCM} can also be temperature dependent, however; furthermore, attack of bromodicyanomethane on **5B** should be less selective at 160°. A $\Delta G^{*}_{cis} - \Delta G^{*}_{trans}$ value of 2·1 kcal/mol (see page 3604) nevertheless gives rise to a *trans/cis* ratio (at 160°) of 11, corresponding to 92% *trans* product. Therefore, all processes with similarly high activation energies, e.g., also those which proceed with participation of boat or twist-boat forms, were neglected in the calculations.

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* For a completely irreversible reaction.

Acknowledgements—This work was supported by the Deutsche Forschungsgemeinschaft, the Stiftung Volkswagenwerk, the Land Niedersachsen, the Fond der Chemischen Industrie and the Universitätsbund Göttingen. We also thank Profs. Drs. H. Brockmann and W. Lüttke for financial support and Miss J. Etzemüller for technical assistance.

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