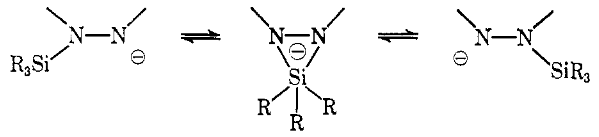
$(BH)_e(A^-)$, it follows that $k_1(B^-) \cong k_2(A^-)$. Independent information about the ratio $(A^-)/(B^-)$, not presently available, would be necessary in order to obtain actual values of k_1 and k_2.

Reaction Mechanism. Results of the kinetic experiments are generally consistent with the model proposed in eq 1, in which equilibration of hydrazine isomers is effected by deprotonation, anion rearrangement, and reprotonation. Other 1,2 anionic rearrangements are known,[6] but none have been found to proceed catalytically as the hydrazine rearrangement does. Most anionic rearrangements involve movement of a substituent from one kind of atom to another kind, the best known being the Stevens (N → C) and Wittig (O → C) rearrangements. Such rearrangements generally proceed irreversibly to produce a much more stable anion and are usually quite slow. The other reaction most closely related to ours is the C → C rearrangement of substituted ethanes, discovered independently by Grovenstein[8] and Zimmerman.[9,10] The kinetics of this reaction have not been studied, but it is clearly much slower than rearrangement of the silylhydrazide anions. In fact, we estimate that the silylhydrazine rearrangement proceeds, at the minimum, 10^6 faster than any previously known anionic rearrangement.

In intramolecular 1,2 anionic rearrangements, the transition state is thought to involve bridging by the migrating group, which must at some point be equally bonded to the 1 and 2 atoms. The energy of activation for migration of an organosilicon substituent could be much less than for other bridging groups, because of the availability of 3d orbitals on silicon which permit easy expansion of covalence from four to five.[11]



These considerations suggest that silyl groups should be exceptionally mobile in other anionic rearrangements, a possibility which is now being tested.

Acknowledgment. M. I. thanks the United States Educational Commission (Japan) for a travel grant.

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(8) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).

(9) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).

(10) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(11) There is much indirect evidence for pentacoordinate intermediates in organosilicon chemistry, and at least one stable pentacoordinate triorganosilicon species has been isolated;[12] see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(12) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963).

Skeletal Rearrangements of the Methyl-7,7-dicyanonorcaradienes[1]

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received March 23, 1967*

Abstract: Skeletal rearrangements of methyl-substituted 7,7-dicyanonorcaradienes occur at temperatures above 55° and are shown to be intramolecular. Isotopic position-labeling experiments are consistent with a circumambulatory mechanism. The major competing process is aromatization, which seems to be fast enough to prevent observation of any significant amount of cyano group shift. The drastic reduction (*ca.* 18 kcal/mole) in activation energy for the circumambulatory process produced by changing 7,7-dimethyl to 7,7-dicyano substitution is attributable to elimination of the endothermic preliminary tropilidene → norcaradiene step and to weakening of the C-1–C-7 bond in the cyano cases.

At temperatures near 300°, skeletal rearrangements interconvert *x*,7,7-trialkyltropilidenes (cycloheptatrienes) by way of a mechanism that probably involves preliminary valency tautomerism to the corresponding norcaradienes (bicyclo[4.1.0]heptadienes).[3,4] The endothermic preparatory step adds an estimated 7–15 kcal/mole to the activation energy for the skeletal rearrangement. True norcaradienes presumably would not be required to pay this energy increment and therefore should rearrange at much lower temperatures. The recent discovery by Ciganek[5] that the products of reactions of dicyanodiazomethane with aromatic hydrocarbons are 7,7-dicyanonorcaradienes rather than 7,7-dicyanotropilidenes makes possible a test of this question.

The Toluene–Dicyanodiazomethane Reaction. Thermolysis of a solution of dicyanodiazomethane[6–8] in

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(1) The support of this work by grants from the National Science Foundation, the Air Force Office of Scientific Research, and the Army Research Office, Durham, is gratefully acknowledged.

(2) (a) National Institutes of Health Postdoctoral Fellow, 1966–1967; (b) National Institutes of Health Postdoctoral Fellow, 1964–1965.

(3) (a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751 (1965); (b) *ibid.*, **87**, 2752 (1965); (c) *ibid.*, **88**, 2494 (1966).

(4) J. A. Berson and M. R. Willcott, III, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 139 (1966).

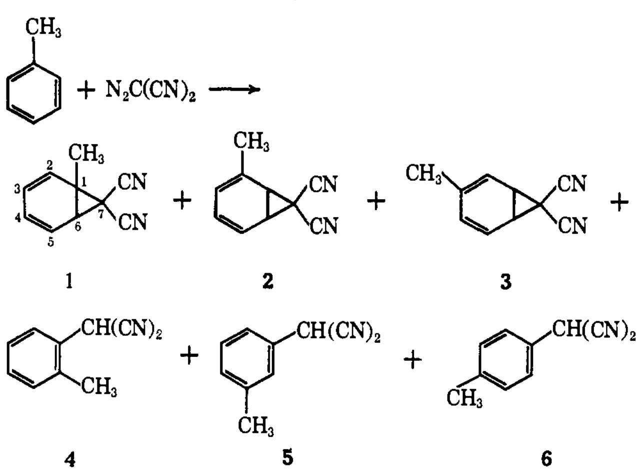
(5) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652, 1149 (1965).

(6) We are greatly indebted to Dr. Ciganek for information on the preparation[7] and reactions[8a] of this material in advance of publication as well as for helpful discussions of the chemistry of the dicyanonorcaradienes.[8b]

(7) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

(8) (a) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454 (1967); (b) *ibid.*, **89**, 1458 (1967).

toluene produces a mixture containing varying amounts of the three *x*-methyl-7,7-dicyanonorcaradienes (**1**, **2**, and **3**) and the three tolylmalononitriles (**4**, **5**, and **6**).

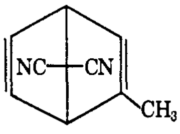


The proportions of the norcaradienes depend upon the history of the sample, since they interconvert appreciably under the conditions of the addition. Aromatization of **1**, **2**, and **3** to **4**, **5**, and **6** occurs upon prolonged heating, as has been observed with other 7,7-dicyanonorcaradienes;[5] this transformation also is effected very readily by exposure to a variety of mild chromatographic adsorption materials. Separations of the mixtures therefore are difficult.

The composition of a typical mixture obtained under conditions chosen to minimize aromatization and interconversion is about 10–20% each of **1** and total aromatics and 40–45% each of **2** and **3**.

The methyl absorptions of **1**, **2**, and **3** in the nuclear magnetic resonance (nmr) spectrum occur at δ 1.65 (singlet), 2.09 (doublet, $J \cong 1.5$ cps), and 1.97 (doublet, $J \cong 1.5$ cps) and permit rather accurate quantitative analysis for the components. Aside from the weak absorption of aromatically bound methyl (δ 2.5) due to the presence of small amounts of **4**, **5**, and **6** (which is matched by an aromatic ring proton absorption at δ 7.35 approximately four-thirds as intense), there are no additional methyl absorptions. The bridgehead and olefinic protons appear as unresolved multiplets near δ 3.24 and 6.2.

Structure of the Adducts. Repeated careful crystallization of the toluene–dicyanodiazomethane product from ether–cyclohexane permits the isolation of the major norcaradiene component, the 2-methyl isomer, **2**, mp 81–82°, in >98% purity, as judged from the nmr spectrum. The nature of the ring system as a norcaradiene rather than a tropilidene is immediately evident from nmr integration, which shows, in addition to the three-proton methyl doublet at δ 2.09, absorption of three olefinic protons near δ 6.2 and two bridgehead protons near δ 3.2. Norbornadiene and bicyclo[3.2.0]-heptadiene structures, *e.g.*, **7** and **8**, both of which would be compatible with the nmr spectrum, are ruled out by the typical[8] 7,7-dicyanonorcaradiene ultraviolet absorption, λ_{max} 275 mμ (ϵ 3500).



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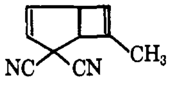

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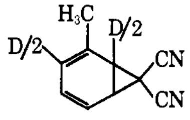
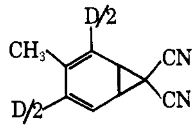
The observed splitting ($J \cong 1.5$ cps) of the methyl absorption of the "crystalline" isomer and the 3:2 intensity ratio of olefinic to bridgehead absorptions are compatible with either structure **2** or **3** but exclude structure **1**, which would show a singlet methyl absorption and a value of 4:1 for the intensity ratio. A choice between structures **2** and **3** is based upon the properties of the deuterium-labeled analogs.

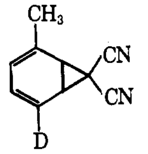
The reactions of *o*- and *p*-deuteriotoluenes with dicyanodiazomethane give mixtures of labeled products from which crystalline norcaradienes can be isolated as in the unlabeled series. These products have solubilities, melting points, and chemical shifts (δ 2.09) of the nmr methyl absorptions which are the same as those of the major "crystalline" isomer in the unlabeled series and thus very probably have the same structure (apart from the isotopic difference). The intensity ratios for methyl, bridgehead, and olefinic proton absorptions in the nmr spectra of the "crystalline" isomers from *o*- and *p*-deuteriotoluene (**2**-*o*-*d* and **2**-*p*-*d*) are 3.00:1.47:2.49 and 3.00:2.02:1.92. If the secondary kinetic isotope effect on the addition is assumed to be negligibly small, the theoretical ratios for the **3** structures are 3:2:2 and 3:1:3, whereas those for the **2** structures are 3:1.5:2.5 and 3:2:2. The observed values agree with the ratios expected for the **2** series, and the "crystalline" norcaradiene therefore is assigned that structure.



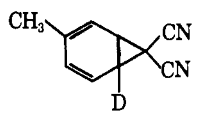
2-*o*-*d*



3-*o*-*d*



2-*p*-*d*



3-*p*-*d*

The evidence on the structures of the other two isomers, **1** and **3**, is circumstantial. Two and only two other norcaradienes are possible in this series, and only two methyl absorptions (other than the doublet of **2**) appear in all the adduct mixtures. Analogy with Ciganek's results[8] in the benzene and xylene series, where other types of adducts are absent, suggests that the two extra toluene adducts are also norcaradienes. That they are not norbornadienes or bicyclo[3.2.0]-heptadienes is indicated by the ultraviolet spectra of mixtures of the three adducts enriched in **1** and **3**. Such mixtures show extinction coefficients about the same as that of pure **2** rather than the depressed values that would be caused by the presence of unconjugated structures. Furthermore, the "crystalline" norcaradiene **2** is reversibly interconverted with the other two (see below). It is difficult to formulate any rearrangement process involving mixtures of norbornadienes, bicyclo[3.2.0]heptadienes, and/or tropilidenes in any proportions that reasonably will afford three and only three isomeric compounds.

Rearrangements and Aromatizations. Interconversions of the three adducts occur slowly in boiling chloroform and readily in boiling carbon tetrachloride (*ca.* 77°). Run 2 in Table I shows the change in composi-

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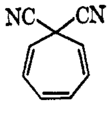
Table I. Thermal Rearrangements of the Methyl-7,7-dicyanonorcaradienes

Run	Time, hr	% composition 1	2	3	Aromatics
1^a	0.0	$<4^d$	>96	$<4^d$	$<4^e$
	1.75	18	64	8	10
2^b	0.0	5	83	8	~5
	0.5	4	78	8	10
	1.5	5	73	11	11
	3.5	6	70	12	11
	5.5	9	66	14	12
	10.0	10	63	14	13
	26.0	10	54	21	15
	31.5	6	63	11	19
	38.5	8	57	12	23
3^b	0.0	23	35	30	12
	1.5	24	32	30	13
	4.0	19	36	31	13
	7.0	15	37	33	15
	20.5	11	44	24	22
	30.5	12	40	23	24
	50.0	8	36	19	37
	70.0	7	33	11	50
4^c	0	5	72	11	12
	5.25	7	74	7	12
	13.75	11	69	9	12
	30.75	12	66	9	13
	39.75	15	61	8	14
5^f	0	34	30	23	18
	24	39	24	12	25
6^g	0	7	81	8	5
	0.5	16	71	4	9
	1.0	17	64	5	14
	1.5	18	57	6	20
	2.25	17	52	7	25
	3.75	14	44	6	36
	5.25	11	31	5	53
	8.25	8	21	4	67
7^g	0	13	26	12	49
	0.5	9	24	4	61
	1.0	7	18	6	69
	1.75	7	16	4	74
	2.75	4	11	2	83
	4.75	...	...	...	88
	7.75	...	...	...	93

[a] In dioxane at reflux. [b] In carbon tetrachloride at reflux. [c] In deuteriochloroform at 55 ± 2°. [d] Total of **1** + **3** methyl peaks too small to observe; less than 4% of **2** methyl peak. [e] Aromatic methyl peak too small to observe; less than 4% of **2** methyl peak. [f] In toluene at 80°. [g] In deuteriochloroform at 100 ± 4°.

tion of such a reaction mixture with time. In this case, the starting material is a mixture heavily enriched in **2** but nevertheless containing some **1** and **3**. Thus, a a mere change in the **2**:**1**:**3** ratio with time need not signify interconversion of the three norcaradienes but might instead result from differing rates of aromatization. Table I shows, however, that this interpretation is untenable because the total amount of aromatization at any time is insufficient to account for the observed shift in composition. For example, if the composition at the 10.0-hr point of run 2 were made up of norcaradienes **1**, **2**, and **3**, which had not interconverted, the largest change from the initial composition would be effected if the only change occurring were aromatization of the initial major component **2**. This would lead to the composition 5% **1**, 75% **2**, 8% **3**, and 13% aromatics. The observed composition is quite different: 10% **1**, 63% **2**, 14% **3**, and 13% aromatics. The decrease in **2** and increase in **1** and **3** cannot be explained by aromatization alone and requires that at least some of the change in composition be attributed to interconversion of the norcaradienes. The situation is even clearer in run 1, where essentially pure **2** is converted to a mixture containing substantial amounts of **1** and **3**, and in run 4, where little or no aromatization occurs but the composition of the norcaradiene mixture shifts markedly.

Run 3 shows the reversibility of the norcaradiene rearrangements. Again, the total amount of aromatization at a given point is insufficient to account for the change in the **1**:**2**:**3** ratio. At 20.5 hr, for example, if norcaradiene interconversions are excluded, the closest approach to the experimental figures is achieved by the assumption that aromatization of **1** is fast relative to that of **2** or **3**. The calculated composition is then 13% **1**, 35% **2**, 30% **3**, and 22% aromatics, a rather poor fit to the observed values, 11% **1**, 44% **2**, 24% **3**, and 22% aromatics. Furthermore, attempts to explain the shifts in product ratios by aromatization alone run into the paradox that the relationship of the rates of aromatization (**2** > **1**) needed to explain runs 2 and 5 is the reverse of that needed to explain run 3 (**1** > **2**).



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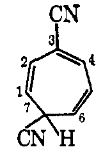

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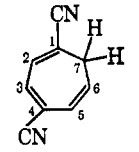

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The cyano group shifts which Ciganek observed[8] to occur at higher temperatures with 7,7-dicyanonorcaradiene itself seem to be indetectable with the methyl-substituted series examined here. The nmr spectra of the rearrangement mixtures show no absorptions in the vinyl region further upfield than $\delta = 5.8$ ppm. The 7,7-dicyanonorcaradienes all show vinyl proton absorption in the region $\delta = 5.8$–6.5 ppm, whereas the 3,7-dicyanotropilidenes that would result from a 7- → 3-cyano group shift (*e.g.*, **9** → **10**) show vinyl proton absorption at higher field attributable to protons at C-1 and C-6.[8] Furthermore, our reaction mixtures show no absorption near $\delta = 2.7$ ppm, a region characteristic[8] of the C-7 protons in the 1,4-dicyanotropilidenes that result from a 7- → 4-hydrogen shift (*e.g.*, **10** → **11**) in the 3,7-dicyanotropilidenes.[8] Even at 100°, the cyano-group shift is not observed in the methyl-substituted series. It seems likely that the difference in behavior between the present cases and those where the shift occurs[8] results from a change in the ratios of the rates of cyano group shift and aromatization. Ciganek[8] reports a first-order rate coefficient of 2.17×10^{-6} sec^{-1} for the aromatization of 7,7-dicyanonorcaradiene to phenylmalononitrile in deuteriochloroform at 100°. This rate is only about 1.5 times as fast as the cyano group shift, which is therefore readily observable. Under the same conditions, aromatization in the methyl-7,7-dicyanonorcaradienes (**1**, **2**, and **3**) seems to be considerably faster. Although the kinetics are complicated by the skeletal rearrangement, the over-all aromatization process obeys a first-order rate law at 100° rather well when the initial composition is close to that of an apparent steady-state mixture (about 23% **1**, 66% **2**, and 11% **3**). The data for aromatization of a mixture with an initial composition not far from

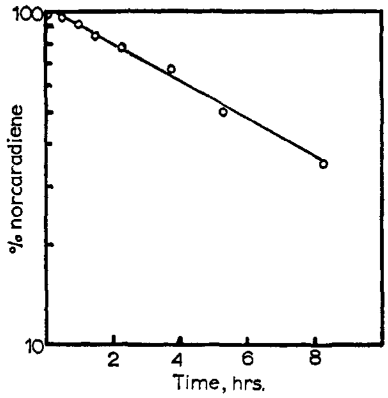
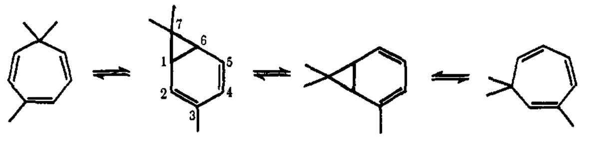


Figure 1. Aromatization of a norcaradiene mixture with initial composition near the "steady-state" value (run 6, Table I).

this (run 6, Table I) are plotted in Figure 1. The resulting composite rate coefficient is 3.5×10^{-5} sec^{-1}. When the initial mixture is enriched in **1** (run 7, Table I), the first-order rate coefficient drifts downward until about the same 23:66:11 steady-state composition is reached, by which time it is approaching the above value, 3.5×10^{-5} sec^{-1} (Figure 2). This steady-state aromatization rate for the methyl-substituted case is about 16 times the aromatization rate[8] of the parent compound, 7,7-dicyanonorcaradiene. Thus, even if the absolute rate of cyano-group shift in the methyl series (**1**, **2**, and **3**) were about the same as that of the parent compound, the faster aromatization process would drain away the bulk of the material irreversibly before the cyano-group shift had manifested itself. The rather pronounced substituent effect favoring aromatization in this competition seems worthy of further examination.

Detailed Structural Aspects of the Rearrangements. Previous isotopic marking studies[3,4] showed that the sequential arrangement of the atoms C-1 through C-6 remained unchanged throughout the rearrangements of the *x*,7,7-trimethyltropilidenes. The simplest mechanism consistent with these and other observations[3,4] involved norcaradienes which were capable of interconverting by migration of C-7 from C-6 to C-2, with C-1 acting as a pivot point. Several alternative intermediates were excluded.



Although the present system is less readily adapted to labeling patterns that are highly sensitive to the details of mechanism, the results of the rather crude marking experiments to be described are fully consistent with the direct norcaradiene interconversions postulated to account for the previous observations[3,4] in the trimethyltropilidene series.

Scheme I shows that direct interconversion of the deuterium-labeled methyl-7,7-dicyanonorcaradienes by the circumambulatory mechanism[3,4] leaves the positions of the labels unchanged from those established in the synthesis from *o*-deuteriotoluene. (In Scheme I, each heavy dot represents a position bearing, on the average, half a deuterium atom and half a hydrogen.) Thus, even prolonged exposure of a mixture of **1**-*o*-*d*, **2**-*o*-*d*, and **3**-*o*-*d* to the rearrangement conditions should permit reisolation of **2**-*o*-*d* with the original ratio of nmr absorption intensities in the methyl (3.0), bridgehead (1.5), and olefinic (2.5) regions. This requirement is fulfilled when a mixture of 23% **1**-*o*-*d*, 34% **2**-*o*-*d*, 30% **3**-*o*-*d*, and 13% aromatics, synthesized by the reaction of dicyanodiazomethane with toluene-*o*-*d*, is heated in carbon tetrachloride for approximately five half-lives of approach to the "steady-state" mixture. The 2-methyl-7,7-dicyanonorcaradiene reisolated by crystallization shows methyl:bridgehead:olefinic proton absorptions in the nmr in the intensity ratios 3.00:1.54:2.53, in good agreement with the values 3.00:1.47:2.49 observed on a sample isolated before pyrolysis.

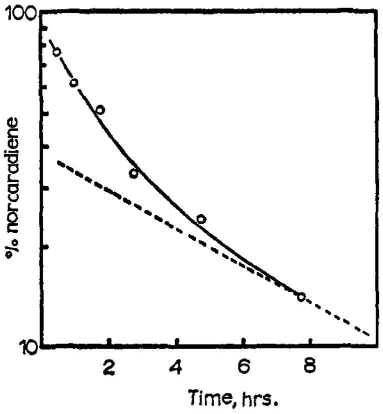
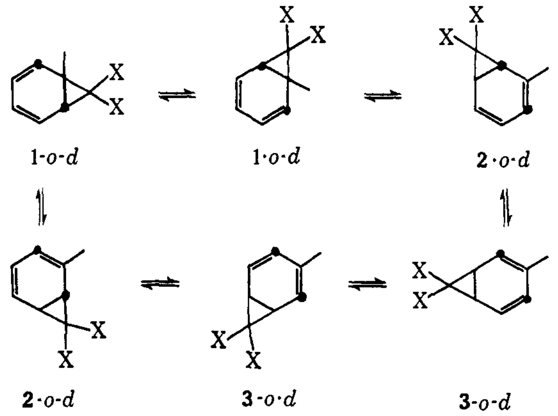


Figure 2. Aromatization of a norcaradiene mixture with initial composition rich in the 1-methyl-7,7-dicyano isomer **1** (run 7, Table I). The slope of the dotted line is the same as that of the line in Figure 1.

Scheme I. X = CN; • = D/2



On the basis of these position-labeling experiments, a mechanism involving reversible fragmentation of **1**-*o*-*d*, **2**-*o*-*d*, and **3**-*o*-*d* to *o*-deuteriotoluene and dicyanocarbene is formally indistinguishable from the circumambulatory mechanism. Fragmentation–recombination is ruled out, however, by the observation that when the rearrangement of the three deuterium-labeled norcaradienes is carried out in ordinary toluene as solvent (at 80°), the recovered mixture of norcaradienes shows a methyl:bridgehead + olefinic proton ratio of 3.00:3.92, essentially unchanged from the ratio 3.00:3.89 found in the starting material. Fragmentation–recombination would have resulted in complete loss of deuterium from the norcaradienes, and the observed

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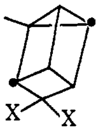
nmr intensity ratio therefore would have been 3:5. The complete retention of deuterium means that no significant part of the rearrangement proceeds by way of an intermolecular mechanism.

The position-labeling results, although consistent with the circumambulatory mechanism, are not decisive. As in the case of the trimethyltropilidene rearrangements,[3,4] interconversion might also be imagined to occur *via* other intermediates such as the homoprismane type (*e.g.*, **12**) or a sequential combination of tropavalene (*e.g.*, **13**) and bicyclo[3.2.0]heptadiene (*e.g.*, **14**) types. Although such species were excluded by labeling experiments in the trimethyltropilidene cases,[3,4] they unfortunately cannot be so dismissed in the present work. Achievement of isotopic equilibrium *via* intermediates like **12** or **13** + **14** would produce 2-methyl-7,7-dicyanonorcaradiene with a statistical distribution of deuterium (**15**), with the label equally spread over the five carbons available. This would result in a methyl: bridgehead:olefinic proton intensity ratio of 3.00: 1.60:2.40 in the nmr, which is almost within experimental error of that predicted (and observed) for the circumambulatory mechanism.



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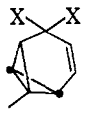

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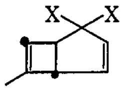

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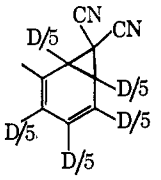
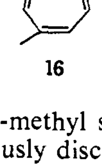
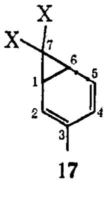


15

Perhaps the best argument against such alternatives is the strongly enhanced rate of the rearrangement in the dicyano series. It is difficult to imagine reasons for the enormous acceleration of these reactions if homoprismane or tropavalene + bicyclo[3.2.0]heptadienes are involved, since the bonds being broken and formed are remote from the site of substitution and should be perturbed only slightly by replacement of methyl by cyano groups. On the other hand, the circumambulatory mechanism (**16** → **17** → **18** → **19**) should be very sensitive to such substitution. Not only should cyano-for-methyl substitution at C-7 of **16** eliminate the previously discussed 7–15 kcal/mole portion of the activation energy associated with norcaradiene formation (**16** → **17**), but also it should have a pronounced effect on the rearrangement step (**17** → **18**) by virtue of the expected strong perturbation of the breaking bond (C-7:C-6). The net effect should be larger than 7–15 kcal/mole by an amount equal to the bond-weakening effect of the two cyano groups.



16



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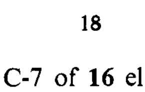
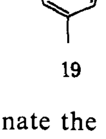


18



19

From the assumption that the effect is mainly on the activation energy and the observation that the rearrangement rate at 300° in the trimethyltropilidene cases[3,4] (half-lives *ca.* 1–2 hr) is roughly the same as that at 80° in the methyl-7,7-dicyanonorcaradiene cases, one calculates that the substitution produces a decrease of about 18 kcal/mole in the over-all activation energy of the rearrangement. This is large enough to suggest that the anticipated energy benefits of preliminary norcaradiene formation and of bond weakening both have been realized.

Experimental Section[9]

Reaction of Dicyanodiazomethane with Toluene. A suspension of 5.32 g (12.0 mmoles) of lead tetraacetate in 40 ml of toluene was cooled to 5° in an ice bath and treated with 1.0 g of carbonylcyanide hydrazone[7] which was added in small portions during 1–2 min. The mixture was stirred in the cold for 5 min and then at room temperature for 2 hr. Water (7 ml) was added; the mixture was stirred for 5 min, and a brown solid material was removed by filtration through a pad of diatomaceous earth. The yellow organic layer was washed with two further portions of water, filtered again through diatomaceous earth, and dried over magnesium sulfate for 1 hr. The dried solution of dicyanodiazomethane was filtered and then heated for 25 min at 75°. Vigorous gas evolution occurred and then subsided. The reaction mixture was cooled and poured onto a short column of Florisil, and the product was eluted with 200 ml of toluene. Evaporation of the solvent *in vacuo* left a residue which had an nmr spectrum indicating the presence of about 20% **1**, 10% aromatics, 40% **2**, and 30% **3**.

This mixture was taken up in about 10 ml of dry ether and kept at −78° for 3 hr, whereupon a few milligrams of a white crystalline solid separated, mp 81–82°. Recrystallization was effected from ether–cyclohexane. The nmr spectrum showed this material to be a

Table II. Ultraviolet Spectra of Arylmalononitriles and Dicyanonorcaradienes

Compound	$\lambda\lambda_{max}$, mμ (ε)	Ref
2,5-Xylylmalononitrile[a]	276 (800) 268 (750)	*d*
o, *m*, and *p*-Tolylmalononitriles (mixture)[b]	270 (520) 263 (480)	*e*
Methyl *p*-tolylmalonate[c]	272 (320) 265 (280)	*e*
7,7-Dicyanonorcaradienes		
Parent compd[a]	271 (2920)	*f*
2-Methyl[b]	275 (3500) 235 (3200)	*e*
1,4-Dimethyl[a]	276 (2540) 235 (1850)	*f*
2,5-Dimethyl[a]	279 (4900) 238 (3290)	*f*
Mixture[b,g]	275 (3540) 235 (3230)	*e*
Mixture[b,h]	275 (3390) 235 (3230)	*e*
Mixture[b,i]	275 (3570) 235 (3200)	*e*

[a] In cyclohexane. [b] In acidified 95% ethanol. [c] In ethanol. [d] Reference 8b. [e] Present work. [f] Reference 5. [g] 12% tolylmalononitriles, 5% **1**, 72% **2**, 11% **3**. [h] 17% tolylmalononitriles, 15% **1**, 61% **2**, 10% **3**, obtained by thermal treatment of the preceding mixture. [i] 5% tolylmalonitriles, 7% **1**, 81% **2**, 8% **3**.

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(9) Nmr spectra were taken with a Varian A-60 instrument. Chemical shifts are given in parts per million and are measured downfield from tetramethylsilane as internal reference. Microanalyses were performed by Microtech Laboratories, Skokie, Ill. Infrared spectra were taken with Perkin-Elmer Infracord or Beckman IR-8 spectrometers. Ultraviolet spectra were taken with a Cary Model 11 or 15 spectrophotometer.

mixture of 91% **2** (methyl absorption at δ 2.09), 5% **3** (methyl absorption at δ 1.97), and 4% **1** (methyl absorption at δ 1.73).

Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.80; H, 5.22; N, 18.03.

In subsequent preparations, samples containing no more than 2–4% **1** and **3** were obtained.

If the pyrolysis of dicyanodiazomethane in toluene was allowed to proceed at reflux for extended periods, the product was almost entirely a mixture of the tolylmalononitriles. Hydrolysis and decarboxylation was effected by heating with 60% aqueous sulfuric acid for 6 hr at 120–150°. Dilution with water, extraction with ether, and concentration gave a mixture of tolylacetic acids. The nmr spectrum in carbon tetrachloride showed a carboxyl proton (δ 11.2, 1 H), aromatic protons (δ 6.95, 4 H), methylene protons (δ 3.35, 2 H), and methyl protons (δ 2.15, 3 H). A small amount of impurity was present as evidenced by a weak absorption (δ 1.1, <1 H). Esterification with diazomethane gave a mixture of the three methyl tolylacetates, identified by comparisons of retention times with those of authentic samples on a Ucon Polar vpc column, 6 mm × 4.4 m, at 175°.

The ultraviolet spectra of mixtures of the tolylmalononitriles were concentration dependent. In 95% ethanol the spectra showed sharply detailed bands at 263 and 270 mμ and a broad band at 290 mμ. The extinction coefficient of the 290-mμ band increased with decreasing concentration and was completely eliminated by addition of a trace of hydrochloric acid. The long-wavelength band thus seems to be attributable to ionization of the malononitrile to the corresponding anion. The data reported in Table II for the tolylmalononitriles and for the samples of norcaradienes containing varying amounts of aromatics were therefore taken on solutions containing *ca.* 0.01 *M* hydrochloric acid, which was more than sufficient to suppress the ionization, and the extinction coefficients for the norcaradienes are corrected for the weak tolylmalononitrile absorption. The spectra of the norcaradienes closely resemble those reported[6,8b] for other norcaradienes. Table II shows that there is no significant change in spectral properties of mixtures of the three norcaradiene isomers **1**, **2**, and **3** as the proportions change.

The rearrangements were followed by nmr spectroscopy. Initial concentrations were about 1–3%. In runs 1 and 5 (Table I), the composition was determined after evaporation of the solvent (dioxane or toluene) *in vacuo* and dissolution of the residue in deuteriochloroform at a convenient concentration. In runs 6 and 7, samples were sealed under nitrogen in nmr tubes and immersed in an oil bath at 100 ± 4°.

Reactions of dicyanodiazomethane with *o*- and *p*-deuteriotoluenes were carried out as in the undeuterated series. The deuterated toluenes were prepared by quenching solutions of *o*- and *p*-tolylmagnesium bromides, respectively, with 99.77% isotopically pure deuterium oxide. The *o*- and *p*-bromotoluenes used in the preparations of the Grignard reagents were obtained from Aldrich Chemical Co. and were at least 99% isomerically pure as established by vpc on a 6 mm × 2 m 20% didecyl phthalate-on-Chromosorb P column. Carbonation of the Grignard reagents gave *o*- and *p*-toluic acids, respectively.

Photochemical Interchange of Halogens in Aromatic Compounds. III[1a]

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Abstract: Measurements of the rate of the photochemical reaction, PhBr + $Cl_2 \longrightarrow$ PhCl + Br_2, in carbon tetrachloride solution have been made. The rate is proportional to the square root of light intensity, the halogen concentration, and the bromobenzene concentration over a limited range, but different proportionalities apply at large and at small bromobenzene concentrations. Quantum yields vary from small numbers to as high as 1300 depending upon conditions, and they generally pass through a maximum during the course of the reaction. Substituent effects in the same reaction, as measured by competition experiments, depend upon whether the reagent providing the chlorine is molecular chlorine or bromine chloride. These results are interpreted as contradicting previously postulated mechanisms and as supporting a concerted displacement. The heat of reaction has been found to be 12.2 ± 1 kcal/mole.

In previous papers[3] we have set forth evidence bearing upon the general scope of the photochemical reactions represented by

$$\mathrm{ArX} + \mathrm{X}' \longrightarrow \mathrm{ArX}' + \mathrm{X}$$

and upon the implication of π complexes in the mechanism (or mechanisms) through which reaction takes place. The exact relationships between these reactions and the formally similar thermal reactions observed at high temperatures by Levine and Noyes[4] and by Engelsma and Kooyman[5] are not yet clear, but certain differences are becoming apparent.

The results reported previously have been concerned in the main with relative measurements of substituent effects, which were obtained in nonchain reactions, such as the reactions of bromine with iodobenzenes or iodine chloride with bromobenzenes, as well as in the chain reactions of chlorine with bromobenzenes. In this report we turn our attention to measurement of the absolute rate of the reaction of bromobenzene with chlorine in moderately dilute carbon tetrachloride solution, a system which we have shown previously[3] to give quantitative yields at room temperature under ir-

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[3] B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Am. Chem. Soc.*, **84**, 158 (1962); B. Milligan and R. L. Bradow, *J. Phys. Chem.*, **66**, 2118 (1962).

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[5] J. W. Engelsma and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 537 (1961).