by ir and melting point comparison with an authentic sample.[26] A red oil was also obtained, but not identified.

Dimerization of 1 with Aluminum Chloride.—To a solution of 2.84 g (0.01 mol) of **1** in 20 ml of carbon disulfide at 23° was added 0.67 g (0.005 mol)[48] of $AlCl_3$. After stirring for 24 hr, distilled water was added, and the product was extracted with CCl_4. The crude product was chromatographed on a 40-cm column of silica gel. Elution with hexane gave as the first fraction a small amount of **1** and approximately 0.4 g of **2**. A second larger red band consisted of a mixture of **20** and **21** (0.9 g, 46% yield). The latter two compounds were separated by recrystallization from ethyl acetate. Compound **20** was a colorless solid: mp 262° dec; ir (KBr) 6.29 (s), 8.07 (s), 8.34 (w), 9.66 (m), 10.70 (w), 10.97 (s), 12.02 (w), 12.81 (m), 13.52 μ (s).

Anal. Calcd for $C_{12}Cl_{12}$: C, 25.30; Cl, 74.70. Found: C, 25.14; Cl, 75.00.

Compound **21** is a stable red solid: mp 185–186°; ir (KBr) 6.36 (s), 6.44 (s), 7.85 (s), 7.93 (s), 8.22 (m), 10.33 (m), 10.82 (s), 11.53 (m), 13.92 μ (w); mass spectrum (75 eV) *m/e* 494 (M), 459 (M − Cl), 424 (M − Cl_2, base ion), 354 (M − Cl_4), 282 (M − Cl_6).

Anal. Calcd for $C_{12}Cl_{10}$: C, 28.90; Cl, 71.10. Found: C, 28.65; Cl, 71.40.

Registry No.—**1,** 6317-25-5; **3,** 25329-35-5; **4,** 6928-57-0; **5,** 33065-95-1; **6,** 33065-96-2; **7,** 33122-14-4; **10,** 33065-97-3; **11,** 33065-98-4; **16,** 33061-05-1; **18,** 33065-99-5; **19,** 309-00-2; **20,** 33066-00-1; **21,** 33061-04-0.

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[48] Larger ratios of **1** to $AlCl_3$ yield larger amounts of **21** and **2** at the expense of **20**.

Protonation and Deuteration of the Isopropenylcyclopentadienyl Anion. Trapping of the Isomeric Product Mixture[1]

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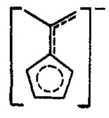
Protonation of the isopropenylcyclopentadienyl anion (**1**) gave a mixture of 15 ± 3% dimethylfulvene (**2**), 58 ± 3% 1-isopropenyl-1,3-cyclopentadiene (**3**), and 25 ± 2% 2-isopropenyl-1,3-cyclopentadiene (**4**). Deuteration of **1** afforded a mixture of 10 ± 4% **2**, 64 ± 3% **3**, and 26 ± 2% **4**. Mass spectral evidence indicates that a lower limit of 97% of the total product mixture was derived from reactions of **1**, while 3% of the product mixture was residual, un-ionized **2**. Chemical trapping of the isomeric product mixture as Diels–Alder adducts of tetracyanoethylene was accomplished. Isomers **2**, **3**, and **4** gave on treatment with tetracyanoethylene adducts 7-isopropylidene-5,5,6,6-tetracyanonorbornene (**6**), 3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (**7**), and 2-isopropenyl-5,5,6,6-tetracyanonorbornene (**8**), respectively. The relative amounts of **6**, **7**, and **8** were within experimental error of the relative amounts of **2**, **3**, and **4**, in the mixtures from which the adducts were derived.

Hine and Knight[3] recently reported a study of the protonation of the isopropenylcyclopentadienyl anion (**1**) derived from the treatment of 6,6-dimethylfulvene



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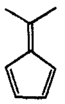
(**2**) with base. Kinetic control of the protonation was hoped for but was not conclusively demonstrated, largely because they did not show whether or not the dimethylfulvene present in the product mixture composed of **2**, 1-isopropenyl-1,3-cyclopentadine (**3**), and 2-isopropenyl-1,3-cyclopentadiene (**4**) was derived from **1** or was **2** that never was ionized.



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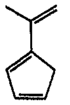

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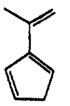

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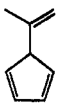

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We have repeated part of this work and in addition report here a detailed study of the deuteration of **1**. Also we succeeded in chemically trapping the thermally unstable (due to Diels–Alder addition) mixture of **2**, **3**, and **4** as Diels–Alder adducts of tetracyanoethylene (TCNE).

Results and Discussion

Several repetitions of the isomerization of dimethylfulvene *via* protonation of anion **1** gave product mixtures in which the relative amounts of **2**, **3**, and **4** were in good agreement with previous work.[3] Table I summarizes the results of seven experiments in which anion **1** was deuterated.

TABLE I

DEUTERATION OF ISOPROPENYLCYCLOPENTADIENYL ANION 1[a]

Run	**2**, %	**3**, %	**4**, %
1	7	63	30
2	8	64	28
3	20	57	23
4	10	64	26
5	9	66	25
6	9	67	24
7	10	65	25
	10 ± 4	64 ± 3	26 ± 2

[a] Equivalent amounts of **2** and potassium *tert*-butoxide in bis(2-methoxyethyl) ether (diglyme) were mixed at room temperature. The homogeneous solution containing anion **1** was added to deuterium acetate in deuterium oxide. Products **2**, **3**, and **4** were quickly extracted into CCl_4 or light petroleum ether and stored at −78° until analyzed. No evidence for the formation of 5-isopropenyl-1,3-cyclopentadiene (**5**) was found.

Relative amounts of **2**, **3**, and **4** in the deuteration–isomerization experiment were determined primarily by nuclear magnetic resonance (nmr) and by gas–liquid partition chromatography (glpc).[4] Deuterium uptake into **3** and **4** should occur at the ring methylene positions

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[1] Delivered in part at the Combined Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970.

[2] (a) Abstracted in part from the M.S. Thesis of R. L. H., University of North Carolina at Greensboro, 1971. (b) National Science Foundation Undergraduate Research Participant, summer, 1970.

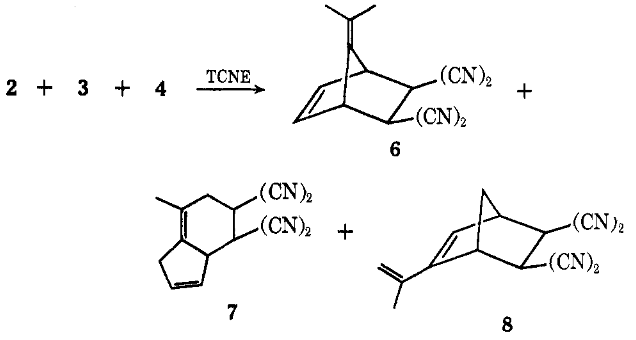
[3] J. Hine and D. B. Knight, *J. Org. Chem.*, **35**, 3946 (1970).

[4] Details of the nmr spectra of **2**, **3**, and **4** are described in ref 3.

of these isomers. In the nmr spectrum of the deuterated isomer mixture in carbon tetrachloride, integration of absorption of the region τ 6.8–7.0, attributed to the ring methylene hydrogens of **3** and **4**, indicated the presence of 1.3–1.4 protons. This is consistent with the uptake of 60–70% of one deuterium into **3** and **4**. The mass spectrum of a sample of deuterated **2**, **3**, and **4** isolated by vacuum distillation indicated the presence of 65–70% of one deuterium in the mixture, within experimental error of the nmr analysis. It was impossible from the nmr spectrum of the deuterated isomer mixture to establish the extent of deuterium uptake into dimethylfulvene due to the overlap of absorptions of **2** with those of **3** and **4**. It was necessary to have an estimate of the extent of deuterium uptake into **2**, however, to confirm that the dimethylfulvene in the product mixture was in fact derived from anion **1** and was not residual, un-ionized **2**. In run 7 (Table I) the deuteration of **1** was carried out and the product mixture was analyzed by gas chromatography–mass spectrometry (gc–ms). Evidence from gc–ms indicated that in the fraction containing **3** and **4** (inseparable by glpc) there was 47% nondeuterated, 50% monodeuterated, and 3% dideuterated product.[5] The dimethylfulvene in the isomerization mixture was 60% nondeuterated, 38% monodeuterated, and 2% dideuterated.

Formation (and uptake of deuterium) of **3** and **4** is presumed to occur *via* reaction of **1**. Likewise, deuterium uptake into dimethylfulvene is presumed to involve reaction of **1**. In this experiment **1** reacted at the ring positions to form **3** and **4** about equally as readily with a proton donor as with a deuteron donor. It is expected that in the same medium the relative amounts of protium and deuterium uptake at the methyl position of **1** would likewise be similar. Hence in **2** derived from **1**, essentially equal amounts of protonation and deuteration are expected to have occurred. Thus 35–40% of the undeuterated **2** is presumed to come from **1**, leaving the possibility that 20–25% of the total dimethylfulvene recovered from the isomerization–deuteration experiment may be **2** that never was ionized by base. An upper limit, therefore, of approximately 3% of the isomerization product mixture is residual, un-ionized dimethylfulvene, while 97% of the mixture is derived from **1**.

Trapping of the Isomers 2, 3, and 4 as Adducts of Tetracyanoethylene.—As the composition of the isomerization product mixture changed on standing at temperatures much above −78°, due primarily to the formation of Diels–Alder adducts among **2**, **3**, and **4**, it was desirable to trap the isomers chemically to give a mixture whose composition was stable with time and which could be isolated. Accordingly, because of its high reactivity as a Diels–Alder dienophile, TCNE was added to the mixture of **2**, **3**, and **4** to trap the isomers as Diels–Alder adducts of TCNE. Of the several possible monoadducts that conceivably could be formed by reaction of TCNE with **2**, **3**, and **4**, only three were observed. 7-Isopropylidene-5,5,6,6-tetracyanonorbornene (**6**) was formed in the reaction of dimethylfulvene with TCNE, while 3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (**7**) formed by the action of TCNE on **3**. The remaining adduct, formed by treatment of **4** with TCNE, was 2-isopropenyl-5,5,6,6-tetracyanonorbornene (**8**).



Tetracyanoethylene acted as an efficient trap for the isomer mixture, as is indicated by the data in Table II.

TABLE II

RESULTS OF TRAPPING ISOMER MIXTURES **2**, **3**, AND **4** AS ADDUCTS OF TCNE

Run	**2**, %	**3**, %	**4**, %	**6**, %	**7**, %	**8**, %
1[a]	11	63	26	7	70	23
2[a]	13	60	27	11	65	24
3[b]	10	64	26	13	59	28
4[b]	9	66	25	8	68	24
	11 ± 2	63 ± 3	26 ± 1	10 ± 3	66 ± 5	25 ± 2

[a] Protonation experiment. [b] Deuteration experiment.

Material balance was not achieved on isolated adducts **6**, **7**, and **8**. Rather, the data in Table II were obtained from integration of nmr spectra of the isomer mixture and also the mixture of adducts. Each of the adducts **6**, **7**, and **8** was isolated and identified by its characteristic infrared and nmr spectra and in the cases of **7** and **8** by elemental analysis. The trapping experiment was also carried out in an nmr tube and the spectrum of the resulting mixture of adducts was exactly the sum of spectra of the individually isolated adducts, allowing estimation of the relative amounts of **6**, **7**, and **8** in the trapped mixture.

Adduct **6** is a known compound, having been reported by Kresze.[6] Adduct **7**, mp 92–93°, showed weak absorption in the infrared at 2245 cm^{-1} characteristic of nitriles having electron-withdrawing groups α to the cyano group.[7] The 100-MHz nmr spectrum of adduct **7** in acetone-d_6 showed absorption in four major bands, τ 8.18, 6.3–7.0, 5.85, and 3.55–3.95 with relative areas of 3.0:4.08:1.05:2.0. The broadened multiplet centered at τ 8.18 consisting of at least four lines was assigned to the methyl group. The basic feature of the absorption in the region τ 6.3–7.0 was a broadened AB quartet, J = 18.0 Hz, centered at τ 6.78. In benzene solution the AB feature was lost and this region showed only two broadened absorptions, each integrating for two protons. Adduct **7**, formed from deuterated **3**, showed a marked decrease in the intensity of the absorption centered at τ 6.78, allowing assignment of this

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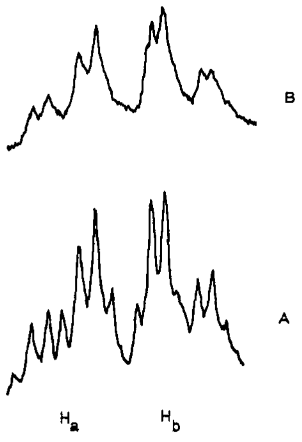
(5) The amount of nondeuterated product observed in this experiment is somewhat higher that that usually observed in the deuteration of **1**. A considerable amount of protonation is not surprising as an equivalent amount of *tert*-butyl alcohol is formed for each mole of **2** ionized (see footnote 13, ref 3), diluting the deuterium pool with protium. The unusually high proportion of nondeuterated product in this experiment is ascribed to the presence of adventitious moisture.

(6) G. Kresze, S. Rau, G. Sabelus, and H. Goetz, *Justus Liebigs Ann. Chem.*, **648**, 57 (1961).

(7) L. J. Bellamy, "Advances in Infrared Group Frequencies," Richard Clay (The Chaucer Press), Bungay, Suffolk, 1968, pp 72–73.



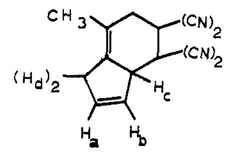


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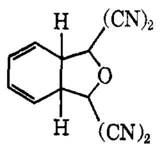
Figure 1.—60-MHz spectra of the vinyl hydrogens H_a and H_b of 3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (**7**): (A) normal spectrum, (B) decoupled spectrum (H_d irradiated).

absorption to H_d. The broadened AB pattern was then assigned to the six-membered ring methylene hydrogens H_e and H_f. Absorption at τ 5.85 was assigned to the methinyl proton, H_c. It is expected that an allylic hydrogen adjacent to geminal cyano groups should be quite deshielded. Support for this chemical shift assignment comes from the report of Linn and Benson[8] that a similar hydrogen in 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydrobenzofuran (**9**) absorbs at τ 5.14.



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On the basis of their low-field appearance the eight-line multiplet centered at τ 3.69 and the seven-line multiplet centered at τ 3.95 (each integrating for one proton) were assigned to vinyl hydrogens H_a and H_b, respectively. Examination of Barton models suggests that a favorable conformation of **7** exists in which the six-membered ring is a half-chair and the four cyano groups at C_4 and C_5 are almost perfectly staggered. This conformation places a cyano group of C_4 in a quasiequatorial position. The dihedral angle between this cyano group and H_b is approximately 27° in this conformation and places H_b within the expected diamagnetic shielding region of the cyano group.[9] Chemical shift assignments for H_a and H_b are made on the expectation that H_b, lying much closer in space to the C_4 quasiequatorial cyano group, should appear at higher field than H_a.

The combined effects of spin decoupling and deuteration in **7** give strong support to the above assignments. Irradiation of the five-membered ring methylene protons, H_d, results in an ABX pattern involving H_a, H_b, and H_c. The AB portion of this pattern is shown in Figure 1. Following the method outlined by Becker[10] which allows hand calculation of the computer-generated solution to the general ABX problem, coupling constants $J_{AC} = -2.03$, $J_{BC} = 2.43$, and $J_{AB} = 6.2$ Hz were derived.

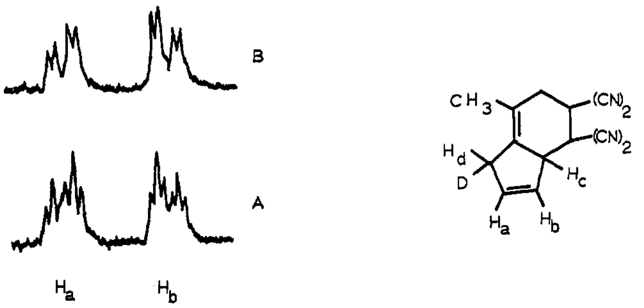


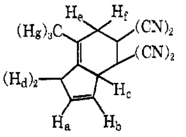
Figure 2.—100-MHz spectrum of the vinyl hydrogens H_a and H_b in 1-deuterio-3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (deuterio **7**): (A) normal spectrum, (B) decoupled spectrum (H_c irradiated).

Irradiation of methinyl H_c at τ 5.85 in deuterated **7** (deuterium at the five-membered ring methylene group) gives rise to an ABX pattern involving H_a, H_b, and H_d, the AB portion of which is shown in Figure 2. Coupling constants $J_{AD} = 2.80$ and $J_{BD} = -1.30$ Hz were assigned.

Four-bond allylic coupling constants are generally negative,[11,12] and the method outlined by Becker[10] indicates that these couplings in **7** are also negative. Irradiation of the methyl group at τ 8.18 causes a simplification of the absorptions due to H_d and also H_e and H_f, indicating coupling extending for four or five bonds. Irradiation of H_c caused an observable alteration of the methyl absorption that was unresolvable due to coupling with methyl by other protons in the molecule. Nmr assignments in **7** are listed in Table III.

TABLE III

CHEMICAL SHIFTS AND COUPLING CONSTANTS IN ADDUCT 7



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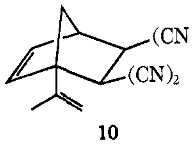
	τ, ppm		J, Hz
H_a	3.69[a]	4.33[b]	$J_{AB} = 6.2$
H_b	3.95	4.55	$J_{AC} = -2.03$
H_c	5.85	6.38	$J_{AD} = 2.80$
H_d	6.78	7.54	$J_{BD} = -1.30$
H_e	3.18 or 3.60	7.79	$J_{EF} = 18.0$
H_f	3.18 or 3.60	7.79	
H_g	8.18	8.93	

[a] 100 MHz in acetone-d_6. [b] 60 MHz in benzene-d_6.

That isomer **3** might have reacted with TCNE to form **10** is not supported by nmr. Also the infrared



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spectrum of the adduct **3** with TCNE lacks absorption in the region 890–910 cm^{-1}, characteristic of terminal

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[8] W. J. Linn and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965).

[9] G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961).

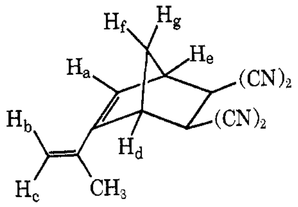
[10] E. D. Becker, "High Resolution NMR, Theory and Chemical Applications," Academic Press, New York, N. Y., 1969, pp 152–159.

[11] M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

[12] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

vinyl groups such as those present in the isopropenyl group of **10**.[13]

Adduct **8**, mp 156–157°, showed weak absorption in the infrared at 2245 cm^{-1} ($C\equiv N$) and strong absorption at 914 cm^{-1} (terminal olefin). The 100-MHz nmr spectrum of **8** in acetone-d_6 showed five separate bands centered at τ 3.50, 4.37, 4.67, 5.31, and 5.67, each integrating for one hydrogen. Present also were multiplets centered at τ 7.76 and 8.08 which integrated for two and three hydrogens, respectively. Chemical shift assignments in **8** were made primarily on comparison with the nmr spectrum of adduct **6**, and also in comparison with 5,5,6,6-tetracyanonorbornene, the adduct of cyclopentadiene and TCNE.



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The broadened doublet (J = 3.2 Hz) centered at τ 3.50 was assigned to H_a, since the vinyl hydrogens of **6** appeared at τ 3.10. The broadened peaks at τ 4.37 and 4.67 were assigned to the isopropenyl vinyl hydrogens H_b and H_c. H_b is expected to appear downfield from H_c due to the anisotropy effects of the norbornenyl double bond.[3] Absorptions at τ 4.37 and 4.67 were assigned to bridgehead hydrogens H_d and H_e. Bridgehead absorption in **6** occurred at τ 4.04. Irradiation of the band at τ 4.67 caused a collapse of the H_a doublet to a broadened singlet. This peak was assigned to H_e since H_e is expected to couple more strongly than H_d with H_a[14,15] and also due to anisotropy effects of the isopropenyl double bond, H_d should be deshielded more than H_e. Absorption centered at τ 7.76 appeared as an AB pattern (J = 11.5 Hz) with each peak showing additional splitting. This pattern was assigned to the bridge methylene hydrogens of **8** (bridge hydrogens of **6** absorbed at τ 8.00). The bridge methylene hydrogens of 5,5 6,6-tetracyanonorbornene also showed an AB pattern, centered at τ 7.83. Numerous other reports of AB patterns arising from nonequivalent geminal bridge hydrogens in norbornene derivatives have been made,[16,17] supporting our assignments in this case. Absorptions at τ 8.08 was assigned to the isopropenyl methyl group.

Estimates of the extent of deuteration of **1** were also obtained from the nmr spectra of **7** and **8**. In isolated samples of **7** and **8** obtained by trapping the deuterated isomer mixture, integration of the region τ 6.3–7.0 in **7** showed the presence of 3.3–3.4 hydrogens while integration of the absorption centered at τ 7.76 in **8** indicated the presence of 1.35 hydrogens. These data indicate the uptake of 60–70% of one deuterium atom into **7** and **8** well within experimental error of other estimates of the extent of deuteration of **1**.

Conclusions

An accurate accounting of the origin of the dimethylfulvene formed in the quenching of the isopropenylcyclopentadienyl anion removes some uncertainties concerning the operation of kinetic control of this process left unresolved in the previous report.[3] However, as we have no direct evidence for the occurrence of **5** in the isomer mixture, it is still uncertain as to whether the mixture, of 10% **2**, 62% **3**, and 27% **4** corresponds to the first formed products. That some rearrangement of the first formed products occurs, probably by a carbanion mechanism, is indicated by the mass spectral observation of the uptake of more than one deuterium atom into the products. To the extent that this secondary ionization occurred, the system would tend toward equilibrium, resulting ultimately in an increase in the relative amount of **2** in the mixture. If changes in the first formed mixture occur only by a carbanion mechanism, the observed product mixture would differ most from that of kinetic control if no **2** were in the first formed mixture, but instead arose from subsequent ionization in the system. Such a rearrangement involving **5** cannot be ruled out by the available evidence. To the extent that **5** is removed from the mixture by a carbanion mechanism, the relative amounts of **2**, **3**, and **4** will increase in the product mixture in a ratio directly proportional to the ratio of the specific rate constants for their formation. If the amount of secondary ionization is minimal, such that the system does not move very far toward equilibrium, the ratio of **2**:**3**:**4** should be independent of the amount of **5** present.

That **5** may have formed on quenching of **1** and then subsequently rearranged by an uncatalyzed sigmatropic hydrogen migration to give **3** remains a possibility. The rearrangement of **5** → **3** must be considerably more rapid than the interconversion of **3** → **4** or **4** → **3**, since the latter processes were fairly slow at room temperature and not observed at all at low temperatures. McLean and Haynes[18] have shown that 5-methylcyclopentadiene is somewhat more reactive than 1-methylcyclopentadiene toward this type of rearrangement. They have also indicated that base-induced rearrangements in alkylcyclopentadienes are much more rapid than uncatalyzed rearrangements in these systems. Since some carbanion formation subsequent to quenching of **1** is indicated in our work, it is likely that the more rapid ionic mechanism would account for virtually all of the loss of any **5** that might have formed in this reaction.

The relative amounts of dimethylfulvene derived from the deuteration of **1** (~8%) indicates that any rearrangement (most reasonably by a carbanion mechanism) of the first formed products was not extensive. Hence, whether or not any **5** was formed in the quenching of **1**, the relative amounts of **2**, **3**, and **4** observed in this work are probably not far removed from the kinetically controlled product ratios.

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[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 26.

[14] R. A. Finnegan and R. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

[15] E. W. Garbisch, Jr., *Chem. Commun.*, 332 (1968).

[16] P. Subramanian, M. Emerson, and N. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

[17] J. D. Davis, Jr., and T. VanAuken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

[18] S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

Experimental Section[19]

Dimethylfulvene (2).—Dimethylfulvene (5-isopropylidene-1,-3-cyclopentadiene) contaminated by 5–10% of dicyclopentadiene was prepared by the method of Freiesleben.[20] 2 was also prepared by the method of McCain[21] using the basic form (hydroxide) of a quaternary ammonium type (polystyrene) anion exchange resin, Amberlite CG-400, as base. This method gives 2 uncontaminated by dicyclopentadiene, but in lower yields.

Isomerization of Dimethylfulvene.—The procedure of Hine and Knight[8] was closely followed in the room temperature isomerization of 2 *via* protonation and deuteration of anion 1. Several repetitions of the protonation experiment afforded product mixtures of 15 ± 3% 2, 58 ± 3% 3, and 27 ± 2% 4. Pmr spectra (60 MHz) were obtained 15–20 min after quenching of the anion. The composition of the product mixture remained essentially unchanged on standing at −78°. Pmr spectra (100 Hz) were obtained after 0.5–2 days' storage at −78°. Dicyclopentadiene (∼5–7%) was used as an internal standard for the glpc analysis.

In a separate experiment dimethylfulvene was also isomerized by the same method with the exception that hexamethylphosphoramide was used as solvent in the place of diglyme. A product mixture of 8% 2, 65% 3, and 27% 4 was obtained in this experiment, indicating little solvent effect on the course of the isomerization.

Deuteration of 1, Gas Chromatographic–Mass Spectral Analysis.—The isomerization was carried out as previously described on 4.02 g of 2 (92.8% 2, 7.2% dicyclopentadiene). The anion was quenched with deuterium acetate in deuterium oxide, extracted into light petroleum ether, and washed with water to remove diglyme solvent. The product mixture was immediately stored at −78° until gc–ms analysis could be made. A $^3/_8$ in. × 6 ft 3% SE-30 on Chromosorb W column at 80° was used for the glpc separation. Retention times of 0.70 (3 and 4, unresolvable), 0.83 (2), and 1.16 min (dicyclopentadiene) were observed. The product mixture contained 8.9% 2, 84.2% a mixture of 3 and 4, and 6.8% dicyclopentadiene. This 5.5% decrease in the relative amount of dicyclopentadiene is within the experimental error of the method (∼10%) and indicated no loss of product. Thus excellent material balance was obtained in this reaction. Mass spectral analyses were made using ionizing potentials of 70 and 19 eV. At 19 eV, peaks due to (parent ion −1) mass unit were almost completely absent. After correction or ^{13}C content,[3] assignments corresponding to 50% C_8H_{10}, 47% C_8H_9D, and 3% $C_8H_8D_2$ for the fraction containing 3 and 4, as well as 60% C_8H_{10}, 38% C_8H_9D, and 2% $C_8H_8D_2$ in the fraction containing 2, were made. The fraction containing dicyclopentadiene had a parent ion of mass 132 corresponding to $C_{10}H_{12}$. On standing at room temperature the sample developed high-boiling components of mass 210–213 corresponding to Diels–Alder adducts involving protonated and deuterated 2, 3, and 4, confirming our suspicions that the composition of the isomeric product mixture may change on standing due to adduct formation involving 2, 3, and 4.

7-Isopropylidene-5,5,6,6-tetracyanorbornene (6).—Equimolar (0.10 mol) amounts of dimethylfulvene and tetracyanoethylene were dissolved in toluene and mixed in a three-necked flask equipped with a nitrogen bleed. A transient dark color was observed which faded quickly, and a solid product separated on standing. The product was recrystallized from acetone at 0° to yield white crystals: mp 133° (lit.[5] 138°); ir (KBr) 2250 cm^{-1} (C≡N); nmr (acetone-d_6) τ 3.10 (t, 2, vinyl), 5.04 (t, 2, bridgehead), 8.15 (s, 6, methyl).

Trapping of Isomers 2, 3, and 4 As Diels–Alder Adducts of TCNE.—The following procedure is typical for several repetitions of the trapping experiment. Some difficulty was encountered in separating the adducts 6, 7, and 8 by fractional crystallization. Material balance was not achieved on isolated adducts but relative amounts of 6, 7, and 8 were determined by integration of the nmr spectra of the total mixture of adducts. The absorptions used in these integrations were not complicated by overlap with other absorptions in the spectra. Peaks used in these estimated were the triplet at τ 3.10 due to the vinyl hydrogens of 6, the multiplet centered at τ 3.95 due to the vinyl hydrogen H_b of 7, and the broadened peak at τ 4.37 due to the downfield isopropenyl vinyl hydrogen of 8.

The carbon tetrachloride solution of 2, 3, and 4 obtained from the protonation or deuteration of 1 was added with stirring to an equimolar amount (0.05 mol) of sublimed TCNE dissolved in 75 ml of acetone under N_2 at 0°. A fleeting dark color was observed to pass through the solution. The mixture was stirred for 10 min and solvent was removed under reduced pressure to give a greenish paste. Excess TCNE (mp 196°) was removed by crystallization from CH_2Cl_2 at 0°. Addition of petroleum ether (bp 60–90°) caused oiling of the product and solvents were again removed under reduced presssure. The residue was dissolved in refluxing toluene–petroleum ether (50:50). On standing several days at 0°, 0.4 g of 3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (7), mp 92–93°, was collected: ir (KBr, in order of decreasing intensity) 762, 670, 1440, 680, 1430, 1105, 2920, 1260, 1380, 1125, 2890, 945, 920, 805, 325, 935, 2830, 1220, 780, 1155, 1250, 3060, 1350, 1045, 425, 1605, 1280, 1315, 610, 445, 840, 2245, 1065, 1065, 1080 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.76; H, 4.31; N, 23.92. Found: C, 71.80; H, 4.33; N, 23.97.

The solvents from the remaining solution were allowed to evaporate at room temperature and, as the mixture became more concentrated, 0.2 g of 2-isopropenyl-5,5,6,6-tetracyanonorbornene (8) was deposited as white crystals: mp 156–157°; ir (KBr, in order of decreasing intensity) 915, 1380, 1280, 1270, 910, 1440, 830, 1570, 3080, 1430, 880, 610, 1620, 2955, 2990, 3005, 1245, 940, 745, 1010, 1030, 2245, 2920, 1180, 1230, 490, 555 cm^{-1}.

Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.76; H, 4.31; N, 23.92. Found: C, 71.49; H, 4.30.

Registry No.—1, 26520-95-6; 2, 2175-91-9; 3, 26385-00-2; 4, 26385-01-3; 6, 33061-12-0; 7, 33061-13-1; 8, 33061-14-2.

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[19] Melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 521 spectrophotometer. Mass spectra were determined using a Varian Model CH-7 spectrometer, and proton nmr spectra were obtained using Varian Models T-60 and HA-100 spectrometers. Elemental analyses were made by Galbraith Laboratories, Knoxville, Tenn.

[20] W. Freiesleben, *Angew. Chem.*, **75**, 576 (1963).

[21] G. H. McCain, *J. Org. Chem.*, **23**, 632 (1958).