

been found. But whatever the mechanism of the substituent interaction, the proportionality found here between ΔH and ΔS (Table III, an isoequilibrium relationship²⁴) suggests that only a single mechanism operates in the systems under study.

The smaller shifts to lower fields (δ values) of the 1,6 protons in the norcaradienes rather than in the cycloheptatrienes are evident here as in previous reports (*cf.* Table IV), consistent with the position of these protons on the cyclopropane ring of the norcaradiene. In the vicinal coupling constants an increase with carbon to carbon double bonding over single bonding is evident; J_{12} and J_{34} are greater for the cycloheptatrienes, J_{23} and J_{25} are greater for the norcaradienes.

Ambiguities in the coupling constants may occur in the analysis of a single spectrum; a test of such an analysis is to use the values obtained from a spectrum at one frequency to calculate the spectrum at another frequency.²⁵ Both 60- and 100-MHz spectra for the 7-*p*-nitrophenyl system were calculated from the values found by analysis of a 220-MHz spectrum; both calculated spectra agreed with the experimental. In

(24) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(25) R. J. Abraham and S. Castellano, *J. Chem. Soc. B*, 49 (1970).

Table IV it will be noted that J_{15} , J_{26} for the cycloheptatrienes is negative; in view of the small magnitude of these couplings, the reality of the negative sign is not certain.

Experimental Section

Nuclear magnetic resonance spectral measurements were made of degassed 10% solutions in deuteriochloroform²⁶ containing TMS as an internal standard in sealed tubes. The 220-MHz spectra²⁷ were recorded with a Varian HR-220 spectrometer equipped with a variable temperature probe,²⁸ the 100-MHz spectra²⁷ with a Varian HA-100 spectrometer, and the 60-MHz spectra with either a Varian A-56/60 or Varian A-60A spectrometer. Decoupled spectra were obtained with a Varian T-60 spectrometer. Analyses were of spectra recorded at 100-Hz sweep widths; spectra were also recorded at greater sweep widths. Frequency calibration was by the side-band technique. The temperature calibration of the 220-MHz instrument was by methanol and ethylene glycol peak separations.

Calculations were done with IBM 360/75 and IBM 360/50 computers.

(26) Some of the 60-MHz spectra were of carbon tetrachloride solutions.

(27) We are indebted to Mr. David H. Live for the 220- and 100-MHz spectra.

(28) This instrument was purchased with the aid of National Science Foundation Grant No. GP8450.

The Cycloheptatriene–Norcaradiene System. III. Dependence of the Ground-State Enthalpy Difference on Substituents in the 7 Position¹

Engelbert Ciganek

Contribution No. 1724 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received July 23, 1970

Abstract: The adducts of phenylcyanocarbene, carbomethoxycyanocarbene, carbomethoxyphenylcarbene, carbomethoxy-*p*-methoxyphenylcarbene, carbomethoxy-*p*-nitrophenylcarbene, and cyano(trifluoromethyl)carbene to benzene have been prepared. Except for the latter, they are crystalline solids that have the norcaradiene structure. In solution, methyl 7-phenyl-7-norcaradienecarboxylate, its *p*-methoxyphenyl and *p*-nitrophenyl analogs, and 7-cyano-7-phenylnorcaradiene are in rapid equilibrium with the corresponding cycloheptatriene valence isomers. The liquid adduct of cyano(trifluoromethyl)carbene to benzene is at room temperature a rapidly equilibrating mixture of 7-cyano-7-(trifluoromethyl)norcaradiene (**2f**, 15%) and 7-cyano-7-(trifluoromethyl)cycloheptatriene (**3f**, 85%), having $\Delta H^\circ = 0$, $\Delta S^\circ = +5$ eu, and E_a for interconversion of about 7 kcal/mol. Raman spectroscopy is shown to be a useful diagnostic method supplementing nmr spectroscopy in the detection of valence isomerizations in the norcaradiene–cycloheptatriene system. Catalytic hydrogenation of **2f/3f** and of ethyl 7-cycloheptatrienecarboxylate gave norcaranes in excess of the amounts expected on the basis of the equilibrium concentrations of norcaradienes in the starting materials.

In previous papers, we reported the synthesis and structure proof,² and some reactions³ of 7,7-dicyanonorcaradiene, the first simply substituted stable norcaradiene. To shed some light on the unexpected stabilization of a norcaradiene relative to the valence isomeric cycloheptatriene by two cyano groups, we varied the substituents in the 7 position and attempted to

estimate the ground-state enthalpy difference for each pair of valence isomers obtained.⁴

Results

Synthesis. All compounds reported here were prepared by addition of the appropriate carbene to benzene; the carbenes were generated by photolysis or

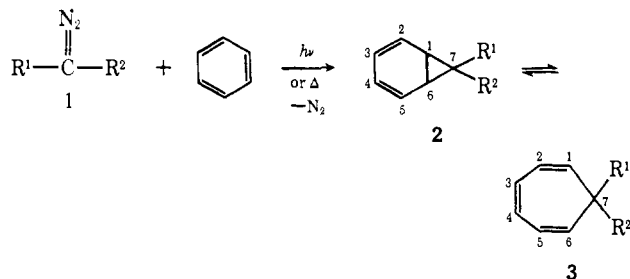
(1) Parts of this paper were reported in preliminary form: E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965).

(2) E. Ciganek, *ibid.*, **89**, 1454 (1967).

(3) E. Ciganek, *ibid.*, **89**, 1458 (1967).

(4) For an estimate of the ground-state enthalpy difference between 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene, see H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970).

thermolysis of the diazo compounds **1**. Thermolysis of phenyldiazoacetone nitrile (**1a**) in benzene gave 7-cyano-7-phenylnorcaradiene (**2a**) in 32% yield. Methyl cyanodiazooacetate (**1b**) did not decompose in refluxing



- a, R¹ = CN; R² = Ph
 b, R¹ = CN; R² = COOMe
 c, R¹ = COOMe; R² = Ph
 d, R¹ = COOMe; R² = *p*-MeOC₆H₄
 e, R¹ = COOMe; R² = *p*-NO₂
 f, R¹ = CN; R² = CF₃

benzene; however, on photolysis methyl 7-cyano-7-norcaradienecarboxylate (**2b**) was obtained in 39% yield. The diazo esters **1c**, **1d**, and **1e** decomposed on pyrolysis in benzene at 120° (but not at 80°); however, a benzene adduct was obtained only in the case of the *p*-nitrophenyl ester **1e**. Photolysis of the diazo esters **1c**, **1d**, and **1e** in benzene, on the other hand, gave the norcaradienes **2c**, **2d**, and **2e** in 31, 17, and 60% yields, respectively. The other products obtained in the photolyses and thermolyses of the diazo compounds **1a–e** in benzene were not identified; they appeared to be mostly the dimers of the corresponding carbenes. Thermolysis of (trifluoromethyl)diazooacetone nitrile in benzene gave a rapidly equilibrating mixture of 7-cyano-7-(trifluoromethyl)norcaradiene (**2f**) and 7-cyano-7-(trifluoromethyl)cycloheptatriene (**3f**) in 77% yield in addition to 2-phenyl-3,3,3-trifluoropropionitrile (**4**; 5% yield). The latter is believed to be the product of direct insertion of cyano(trifluoromethyl)carbene into a C–H bond of benzene since it is not formed on thermolysis of **2f** ⇌ **3f** (see below). The adducts **2a–e** are crystalline solids; **2f** ⇌ **3f** is a fragrant liquid.

Nmr Spectra. The nmr spectrum of 7-cyano-7-phenylnorcaradiene at room temperature in perdeuteriochloroform shows H-1 and H-6 at τ 6.48, characteristic² of the cyclopropyl hydrogens in norcaradienes carrying electronegative groups on C-7. This signal moves to τ 6.77 at –71° and τ 6.32 at +89°, indicating the presence of increasing amounts of the monocyclic valence isomer **3a** in rapid equilibrium with increasing temperatures. This was confirmed by the Raman spectrum (see below). However, it is clear that at all temperatures the norcaradiene **2a** predominates by a large margin, since H-1 and H-6 in **3a** should occur at much lower field.

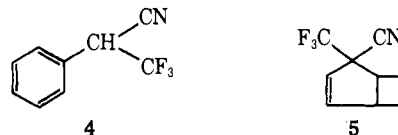
The nmr spectrum of methyl 7-cyano-7-norcaradienecarboxylate (**2b**) is completely independent of temperature (between –70 and +80°) and shows H-1 and H-6 at τ 6.75, indicating the presence of little, if any, of the cycloheptatriene **3b**.

Dissolution of methyl 7-phenyl-7-norcaradienecarboxylate (**2c**) and its *p*-methoxy (**2d**) and *p*-nitro (**2e**) derivatives results in equilibrium mixtures **2** ⇌ **3** whose nmr spectra are strongly temperature dependent. Their analysis has been presented elsewhere. Evidence

(5) G. E. Hall and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2203 (1971).

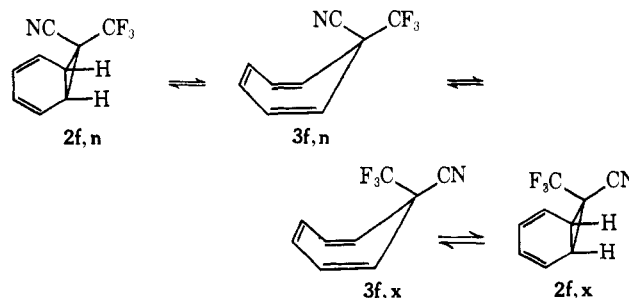
that in the solids only the norcaradienes **2c**, **2d**, and **2e** are present is given below.

The proton nmr spectrum of the adduct of cyano-(trifluoromethyl)carbene to benzene in fluorotrichloromethane at room temperature shows H-2 to 5 as a complex multiplet at τ 3.2–3.8 and H-1,6 as a doublet (separation 7 Hz), split further, at τ 5.30. The position of the latter signal is at lower field than expected for a norcaradiene, but at too high a field for a cycloheptatriene, indicating the presence of a rapidly equilibrating mixture of **2f** and **3f**. This was confirmed by lowering the temperature, which caused the signal at τ 5.30 to broaden, then coalesce, and finally, at below –100°, split up into two new signals at τ 4.60 (doublet, $J = 7$ Hz) and 7.05 (broad singlet with no discernible fine structure, width at half-height 12 Hz). The ratio of peak areas of these signals was 3.45 at –112°. The ¹⁹F nmr spectrum shows similar behavior: a singlet at +73.1 ppm (from the solvent, fluorotrichloromethane) at room temperature changes, on cooling to –112°, to two new singlets at +74.2 ppm and +66.7 ppm in the ratio of 78:22. These spectra show the presence of two species in equilibrium with a rather low barrier for interconversion. The position of the high-field protons shows that the major isomer is the cycloheptatriene **3f** (H-1,6 as a doublet, $J = 7$ Hz at τ 4.60) and the minor isomer the norcaradiene (H-1,6 as a signal at τ 7.05). The nmr spectra of the minor isomer could also conceivably fit a third valence isomer, 4-cyano-4-(trifluoromethyl)bicyclo[3.2.0]hepta-2,6-diene (**5**). However, this structure is ruled out by



the Raman spectrum and the absence of bicyclo[3.2.0]heptane derivatives among the hydrogenation products (see below); the thermal interconversion of **3f** and **5** is also symmetry forbidden.

As in the case of all norcaradienes and cycloheptatrienes carrying two different substituents on C-7, **2f** and **3f** each can exist in isomeric forms having these substituents alternatively in an exo and endo position as shown. Barring the unlikely possibility that the



trifluoromethyl groups of both isomers of **2f** have the same chemical shift, the presence of two signals in the low-temperature ¹⁹F nmr spectrum shows that at that temperature only one of the two isomeric norcaradienes is present, the other signal being due to the cycloheptatriene(s) **3f**. For steric reasons, this isomer is believed to be the one having the much less bulky cyano group in the endo position (**2f,n**). Support for this

assignment also comes from the fact that the only norcarane derivative obtained on hydrogenation of $2f \rightleftharpoons 3f$ is identical with the major product of the addition of cyano(trifluoromethyl)carbene to cyclohexene.⁶ The experimental data available do not exclude the possibility that the other norcaradiene isomer ($2f,x$) is present at elevated temperatures, nor do they allow any definite statement as to the number of cycloheptatrienes present at either -112° or above. Observation of the boat-to-boat inversion of cycloheptatriene itself requires temperatures considerably lower than -112° .⁹ Thus, the signal at $+74.2$ ppm in the low-temperature ^{19}F nmr spectrum of $2f \rightleftharpoons 3f$ may be the averaged signal of the cycloheptatrienes $3f,n$ and $3f,x$, although on steric grounds the isomer $3f,n$ should again predominate. A relevant observation is that further cooling to below -112° caused broadening of only the signal at 74.2 ppm, whereas the width at half-height of the signal at $+66.7$ ppm, assigned to $2f$, remained constant.

The system $2f \rightleftharpoons 3f$ is not too well suited for an accurate determination of the thermodynamic and kinetic parameters,¹⁰ since the relative amounts of the exo and endo isomers of $2f$ and $3f$ present at different temperatures are unknown. Assuming that the exo/endo ratio for each pair of $2f$ and $3f$ remains constant over the whole temperature range, and that the absolute chemical shift of the trifluoromethyl groups in $2f$ and $3f$ is independent of temperature (or changes in the same way as that of the standard, fluorotrichloromethane), one can calculate equilibrium constants $K_{3f/2f}$ for each temperature above coalescence temperature from the equation $K_{3f/2f} = (\delta - \delta_{2f})/(\delta_{3f} - \delta)$, where δ_{2f} and δ_{3f} are the chemical shifts in the absence of exchange and δ the observed averaged chemical shift. In the actual experiment, the averaged signal of the trifluoromethyl group shifted slightly to lower field on cooling, indicating increasing amounts of the norcaradiene present at lower temperatures. The plot of $\ln K_{3f/2f}$ vs. T^{-1} gave a surprisingly good straight line which intersected the point of $K_{3f/2f}$ obtained by integration of the two trifluoromethyl signals at -112° . The ratio of $3f$ to $2f$ at room temperature obtained from this plot was 85:15, the value for -112° was 78:22. The enthalpy difference for the equilibrium $2f \rightleftharpoons 3f$ was calculated to be 0.4 kcal/mol, and the entropy difference $+5$ eu. A similar treatment, using the averaged signal of H-1,6 instead of that of the CF_3 group, gave an erratic plot of $K_{3f/2f}$, indicating that some of the above assumptions may not be correct. However, it is fairly certain that ΔH for this system is close to zero and that $2f$ has the lower entropy. Using the equilibrium constants obtained from the temperature-dependent signal of the CF_3 group, and the

(6) Unsymmetrically disubstituted carbenes usually add to olefins to give the less hindered product; thus, ethyl 7-exo-norcaranecarboxylate is the major product of the addition of carbethoxycarbene to cyclohexene;⁷ cf. also ref 8.

(7) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

(8) R. A. Moss and R. Gerstl, *J. Org. Chem.*, 32, 2268 (1967), and literature cited there.

(9) F. A. L. Anet, *J. Amer. Chem. Soc.*, 86, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, 86, 956 (1964).


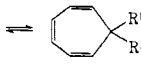
(10) For more sophisticated and accurate determinations of the thermodynamic and kinetic parameters of other norcaradiene-cycloheptatriene systems, see ref 4, 5, and 11.

(11) (a) M. Görlitz and H. Günther, *Tetrahedron*, 25, 4467 (1969); (b) D. A. Kleier, G. Binsch, A. Steigel, and J. Sauer, *J. Amer. Chem. Soc.*, 92, 3787 (1970).

line widths of that signal near coalescence temperature, rate constants for the conversion of $2f$ to $3f$ and for the reverse process were calculated¹² for a number of temperatures and from these, an activation energy of 6.7 kcal/mol for the process $2f \rightarrow 3f$ and 6.4 kcal/mol for $3f \rightarrow 2f$ was obtained. An activation energy of 7 kcal/mol has been reported for the system 7,7-dicyanorcaradiene \rightleftharpoons 7,7-dicyanocycloheptatriene.^{11a}

Raman Spectra. In the detection of equilibria between species having a low barrier for interconversion, Raman and other forms of spectroscopy using a higher frequency radiation have the advantage of permitting the observation of the spectra of the individual species, superimposed on each other, rather than a weighted average of their spectra as is the case in nmr spectroscopy. The double bond stretching mode of cycloheptatrienes¹³ and norcaradienes is too weak in the infrared spectra to be of any diagnostic value; however, this mode is very intensive in the Raman spectra, and, as Table I shows, appears to be well suited as a means of

Table I. Raman Double-Bond Stretching Frequencies of Norcaradienes and Cycloheptatrienes (in cm^{-1} , Relative Intensities^a in Parentheses)^b

R ¹	R ²	Phase		
H	H	Neat liquid		1530 ^c
CN	H	CHCl ₃		1535 ^d
CN	CN	CHCl ₃	1568 ^d	
CN	COOMe	CH ₂ Cl ₂	1563	
CN	Ph	CH ₂ Cl ₂	1565 (100)	1540 (32) ^e
		Solid	1560 (100) ^f	
COOMe	Ph	CH ₂ Cl ₂	1559 (100)	1538 (55) ^g
		Solid	1556 (100) ^h	
COOMe	<i>p</i> -MeOC ₆ H ₄	CH ₂ Cl ₂	1559 (100)	1541 (62) ⁱ
		Solid	1555 (100) ^j	
COOMe	<i>p</i> -O ₂ NC ₆ H ₅	CH ₂ Cl ₂	1558 (100)	1538 (43) ^k
		Solid	1558 (100) ^l	
CN	CF ₃	Neat liquid	1567 (100)	1543 (355) ^m

^a Measured as peak heights. ^b Determined with a Cary 81 helium-neon laser Raman spectrometer. ^c Reference 13. ^d Reference 2. ^e The double bond stretching frequency of the benzene ring is 1605 cm^{-1} (relative intensity 45). ^f Benzene ring: 1606 cm^{-1} (45). ^g Benzene ring: 1605 cm^{-1} (24). ^h Benzene ring: 1604 cm^{-1} (29). ⁱ Benzene ring: 1612 cm^{-1} (52). ^j Benzene ring: 1615 cm^{-1} (40). ^k Benzene ring: 1603 cm^{-1} (182). ^l Benzene ring: 1600 cm^{-1} (185). ^m A band at 1621 cm^{-1} (relative intensity 45) is attributed to the benzene ring of the 5% 2-phenyl-3,3,3-trifluoropropionitrile (4) present in the sample of $2f/3f$ used.

detecting valence isomerizations in the norcaradiene-cycloheptatriene system. Thus, the double-bond stretching mode of cycloheptatrienes seems to occur at 1530 – 1543 cm^{-1} , and that of norcaradienes at 1555 – 1568 cm^{-1} . There is one band in these regions in compounds which are known to contain one valence isomer to the virtual exclusion of the other (e.g., cycloheptatriene and 7,7-dicyanonorcaradiene), and two bands where the presence of rapidly equilibrating mixtures of both isomers has been detected by the temperature dependence of the nmr spectra. It is of in-

(12) The rate constants were obtained by matching the experimental spectra with those calculated by a modified Gutowski-Holmes treatment. We are indebted to Professor J. D. Roberts for these calculations.

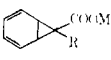
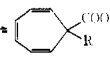
(13) M. V. Evans and R. C. Lord, *J. Amer. Chem. Soc.*, 82, 1876 (1960).

terest to note that in the systems **2a/3a**, **2c/3c**, **2d/3d**, and **2e/3e** both isomers are present in solution whereas the crystals appear to be composed solely of norcaradiene molecules. The lack of a band at *ca.* 1610 cm^{-1} in the system **2f/3f** confirms the absence of the valence isomer **5**: the double bond stretching modes of bicyclo-[3.2.0]hepta-2,6-diene have been observed at 1557 cm^{-1} (cyclobutene double bond, relative intensity 77) and 1607 cm^{-1} (cyclopentene double bond, relative intensity 100).^{14,15}

In an effort to use Raman spectroscopy as a quantitative method of measuring equilibrium constants in the norcaradiene-cycloheptatriene system, the intensity ratios of the bands at 1568 and 1535 cm^{-1} of known mixtures of 7,7-dicyanonorcaradiene and 7-cyanocycloheptatriene in methylene chloride were determined. These were obtained by measuring the peak heights since the widths at half-height of the two bands were identical within experimental error. After correction for the differences in molecular weight, the relative intensity of the double bond stretching band of the cycloheptatriene was found to be 2.0 times that of the norcaradiene in that particular system. Assuming these relative intensities to be independent of substituents at C-7, the ratios of norcaradiene to cycloheptatriene isomers would be 6.3 for the system **2a/3a**, 3.6 (1.8) for **2c/3c**, 3.2 (1.2) for **2d/3d**, 4.6 (1.4) for **2e/3e**, and 0.56 (0.18) for **2f/3f**. The agreement with the values obtained by nmr spectroscopy, given in parentheses, obviously is not very good. The reason for this may be that substituents on C-7 do affect the intensities of the double-bond stretching bands, especially those of cycloheptatrienes, by influencing the geometry of the ring.

Infrared Spectra. The data in Table II indicate that, except for methyl 7-cyano-7-norcaradienecarboxyl-

Table II. Infrared Carbonyl Stretching Frequencies of Methyl 7-Norcaradienecarboxylates and 7-Cycloheptatrienecarboxylates (in cm^{-1})^a

R	Phase		
H	CCl ₄		1750
H ^b	CCl ₄	1720	
CN	CCl ₄	1739	
	Solid (KBr)	1730	
Ph	CCl ₄	1718	1743
	Solid (KBr)	1711	
<i>p</i> -MeOC ₆ H ₄	CCl ₄	1717	1741
	Solid (KBr)	1708	
<i>p</i> -O ₂ NC ₆ H ₄	CCl ₄	1726	1746
	Solid (KBr)	1710	

^a Determined on a Perkin-Elmer 221 prism grating spectrometer.

^b Ethyl 1,2-benzo-7-norcaradienecarboxylate (E. Buchner and S. Hediger, *Ber.*, **36**, 3502 (1903)).

ate, 7-norcaradiene esters show carbonyl frequencies in the range of 1710–1730 cm^{-1} , and 7-cycloheptatriene esters at about 1740–1750 cm^{-1} . Corroborating the Raman spectra, the infrared spectra of the esters **2c/3c**, **2d/3d**, and **2e/3e** show two carbonyl frequencies

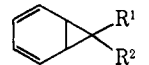

(14) M. V. Evans and R. C. Lord, *J. Amer. Chem. Soc.*, **83**, 3409 (1961).

(15) A band at 1621 cm^{-1} in **2f/3f** is attributed to **4**, known to be present as an impurity (*cf.* footnote *e* in Table I); it appears to be too weak and at too high a wave number to be the stretching mode of the cyclopentene double bond in **5**.

in solution, but only one, characteristic of the norcaradiene esters, in the solid. In addition, the intensities of the two bands in solution are temperature dependent: the norcaradiene ester bands at *ca.* 1720 cm^{-1} predominate at low temperatures, whereas the cycloheptatriene ester bands at *ca.* 1740 cm^{-1} are more intense at elevated temperatures, in agreement with the temperature dependence of the equilibrium constants as observed by nmr spectroscopy.⁵

Reactions

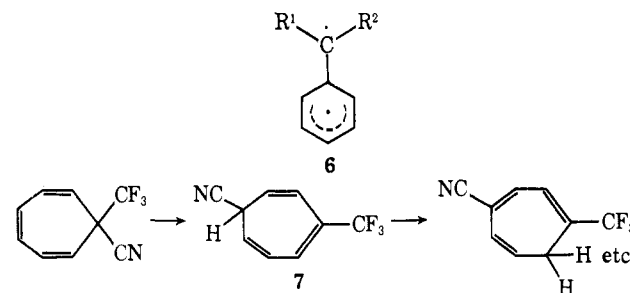
Thermolysis. Table III shows the results of the thermal decomposition of the norcaradiene-cyclo-

Table III. Half-Lives^c of  \rightleftharpoons 

R ¹	R ²	Temp, °C	Half-life, ^a hr	Products
CN	Ph	135	8	Ph ₂ CHCN (70); (cyano)phenylcycloheptatrienes (30) ^b
CN	COOMe	121	9	PhCH(CN)COOMe
COOMe	Ph	159	50	Ph ₂ CHCOOMe
COOMe	<i>p</i> -MeOC ₆ H ₄	159	38	Ph(<i>p</i> -MeOC ₆ H ₄)CHCOOMe
COOMe	<i>p</i> -O ₂ NC ₆ H ₄	159	5	Ph(<i>p</i> -O ₂ NC ₆ H ₄)CHCOOMe
CN	CF ₃	159	3	Cyano(trifluoromethyl)cycloheptatrienes ^b

^a Determined by nmr spectroscopy. ^b See text. ^c In CDCl₃.

heptatriene systems discussed in this paper. With one exception, the thermolysis was studied at one temperature only. In all but the system **2f/3f** (R¹ = CN; R² = CF₃), the major products are those of aromatization, a reaction common to most norcaradienes and cycloheptatrienes.³ The ease of rearrangement correlates with the degree of stabilization of the intermediate diradical **6** by the substituents R¹ and R².



The thermolysis of 7-cyano-7-(trifluoromethyl)norcaradiene/7-cyano-7-(trifluoromethyl)cycloheptatriene (**2f/3f**) was studied at four temperatures (143–168°). No aromatization (to form **4**) occurred; instead, the first step appeared to be a 1,5 shift of the cyano group with formation of **7**, followed by successive 1,5-hydrogen shifts. Such cyano shifts have been observed previously³ in the thermolysis of 7,7-dicyanonorcaradiene. Unlike in that case, the first intermediate (**7**) could not be isolated from the thermal decomposition of **2f/3f** since the subsequent hydrogen shifts were more rapid. However, the intermediacy of **7** was indicated by the fleeting appearance, after a short period of heating, of a triplet ($J = 6$ Hz) at τ 6.9 in the nmr spectrum. The disappearance of **2f/3f** followed first-

Table IV. Products of the Catalytic Hydrogenation of 7-Cyano-7-(trifluoromethyl)norcaradiene/7-Cyano-7-(trifluoromethyl)cycloheptatriene and Ethyl 7-Cycloheptatrienecarboxylate

Catalyst	8	9	10	exo-11	12	13
Rh/C	73	12	15	16	84	0
Pt	17	11	72	13	86	1
Pd/C	23	35	42	4	93	3

order kinetics, giving an activation energy E_a of 30.8 ± 2.4 kcal/mol from which $\Delta H^\ddagger = 30.0$ kcal/mol and $\Delta S^\ddagger = -8.8$ eu were calculated (at 159°). These values compare with $\Delta H^\ddagger = 27.6$ kcal/mol and $\Delta S^\ddagger = -12.2$ eu for the cyano shift in 7,7-dicyanonorcaradiene.³ Since in the latter case part of the activation energy is required to overcome the large ground-state enthalpy difference⁴ between 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene (which is zero for **2f/3f**), the activation barrier for cyano shifts is considerably higher for 7-cyano-7-(trifluoromethyl)cycloheptatriene than for 7,7-dicyanocycloheptatriene. Cyano shifts (in addition to aromatization) were also observed in the thermolysis of 7-cyano-7-phenyl-norcaradiene. Interestingly, no such shifts occurred in methyl 7-cyanonorcaradienecarboxylate (**2b**). The rate of aromatization of **2b** ($t_{1/2} = 9$ hr at 121°) is the same as that of 7,7-dicyanonorcaradiene ($t_{1/2} = 10$ hr at 121°)³ so that the reason for the absence of cyano shifts in the pyrolysis of **2b** must be either a higher ground-state enthalpy difference between **2b** and **3b** and/or a higher activation barrier for cyano shifts in **3b**.

Hydrogenation. Catalytic hydrogenation of 7-cyano-7-(trifluoromethyl)norcaradiene/7-cyano-7-(trifluoromethyl)cycloheptatriene gave 7-cyano-7-(trifluoromethyl)norcarane (**8**, one of the two possible isomers), 1-cyano-1-(trifluoromethyl)cycloheptane (**9**), and 2-cyclohexyl-3,3,3-trifluoropropionitrile (**10**) in ratios depending on the catalyst used (Table IV). The structure of **8** was determined by independent synthesis; it proved to be identical with that of the major product of the addition of cyano(trifluoromethyl)carbene to cyclohexene, which is believed to be the norcarane having the more bulky trifluoromethyl group in exo position (see above). The structures of **9** and **10** were deduced from their molecular weights and spectral properties (see Experimental Section). Although the cycloheptatriene valence isomer **3f** predominates at room temperature by a ratio of 85:15, the products formed on hydrogenation are mostly those derived from the norcaradiene **2f**, namely **8** and **10**. The cyclohexyl derivative **10** must have been formed by hydrogenolysis of the bond between C-1 and C-7 in the norcaradiene **2f** or in the corresponding norcaradiene since the norcarane **8** is stable to further hydrogenation. The apparent higher rate of hydrogenation of the norcaradiene may be the result of differences in the rate of adsorption of the two species on the surface of the catalyst: this rate might be expected to be larger for the planar cyclohexadiene system of the norcaradiene than for the nonplanar triene system of the cycloheptatriene.

These results prompted an investigation of the catalytic hydrogenation of other cycloheptatrienes. Under conditions where hydrogenolysis is minimized (rhodium catalyst), cycloheptatriene gave only cycloheptane;

the presence of 0.005% of norcarane could have been detected. Similarly, 7-cyanocycloheptatriene gave only cyanocycloheptane, but since authentic samples of the 7-cyanonorcaranes were not available, a definite statement as to the absence of these among the hydrogenation products cannot be made. Hydrogenation of ethyl 7-cycloheptatrienecarboxylate, on the other hand, gave mixtures containing up to 16% ethyl *exo*-7-norcaranecarboxylate (**11**) in addition to ethyl cycloheptanecarboxylate (**12**) and traces of the hydrogenolysis product, ethyl cyclohexylacetate (**13**, Table IV). The endo isomer of **11** was absent within limits of detection by gas chromatography. These results seem to indicate that the equilibrium concentration of ethyl 7-norcaradienecarboxylate in ethyl 7-cycloheptatrienecarboxylate is larger than that of norcaradiene in the parent cycloheptatriene, although in both cases the amounts of norcaradienes are too small to be detected directly by any method currently available.

Discussion

The thermodynamic parameters of the norcaradiene-cycloheptatriene systems studied by others and us are compiled in Table V. In addition, the norcaradienes

Table V. Ground-State Enthalpy and Entropy Differences of Norcaradiene-Cycloheptatriene Systems

R ¹	R ²	ΔH° , kcal/mol	ΔS° , eu	Ref
CN	CN	6 ^a		4
CN	COOMe	>4 ^b		This work
CN	Ph	3-5 ^c		This work
COOMe	Ph	5.4	16.8	5
COOMe	<i>p</i> -MeOC ₆ H ₄	2.3	7.4	5
COOMe	<i>p</i> -O ₂ NC ₆ H ₄	3.5	11.0	5
CN	CF ₃	0.4	5	This work
COOMe	COOMe	0.2	3	11a

^a Estimated ΔH between 7,7-dicyano-1,4-bis(difluoromethyl)-cycloheptatriene and 7,7-dicyano-1,4-bis(difluoromethyl)norcaradiene; see ref 4. ^b Limit based on the temperature independence of the nmr spectrum and the absence of a cycloheptatriene band in the Raman spectrum. ^c Estimate based on the slight temperature dependence of the nmr spectrum and the presence of a cycloheptatriene band in the Raman spectrum.

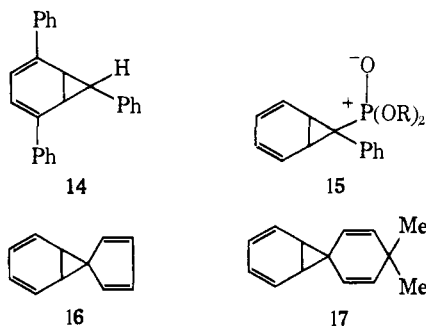
14,¹⁶ **15**,¹⁷ **16**,¹⁸ and **17**¹⁹ recently reported have positive ground-state enthalpy differences with respect to their

(16) (a) T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967); (b) A. Cairncross, to be published.

(17) M. Regitz, H. Scherer, and W. Anschutz, *Tetrahedron Lett.*, 753 (1970).

(18) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

(19) M. Jones, Jr., *Angew. Chem.*, **81**, 83 (1969).



cycloheptatriene valence isomers, although the absolute values have not been determined. Substituents containing π systems appear to be essential for the stabilization of the norcaradiene valence isomer, and, as a rule,²⁰ two such substituents are required; even the cyano group, which seems to be the most effective in this respect, requires the presence of a second substituent to force the equilibrium to the side of the norcaradiene.²¹ There is no correlation of the Hammett σ values with ΔH° ; although the cyano and trifluoromethyl groups have similar σ constants, (+0.66 and +0.54, respectively), they affect the norcaradiene-cycloheptatriene equilibrium in opposite directions.²² Similarly, both methoxyl and nitro groups in the para position of methyl 7-phenyl-7-norcaradienecarboxylate lower the ΔH° with respect to the unsubstituted compound, even though they have σ constants of opposite signs.

Various explanations have been put forward to account for these observations. Calculations show²³ that electronic interaction²⁴ between the cyclopropane ring and acceptor substituents results in a strengthening of the bond between C-1 and C-6 of the norcaradiene by weakening the antibonding contribution of that bond. Another rationalization^{16b,25} is based on the differences in the σ bond energies between differently hybridized carbon atoms:²⁶ such bonds between sp , sp^2 , and sp^3 hybridized substituents and C-7 of the norcaradiene (which as a cyclopropane carbon is approximately sp^2 hybridized) will be stronger than the bonds between the same substituents and the sp^3 hybridized C-7 of the cycloheptatriene. Other factors discussed include dipole-dipole repulsion between substituents on C-7^{2,27} and possible electronic interactions between the endo substituent and the planar diene system of the norcaradiene.² The finding that

(20) The single exception reported to date is **14** where the phenyl groups on C-2 and C-5 should contribute strongly to the stabilization of the norcaradiene.

(21) 7-Cyanocycloheptatriene contains no detectable amounts of 7-cyanonorcaradiene: C. H. Bushweller, M. Sharpe, and S. J. Weininger, *Tetrahedron Lett.*, 455 (1970).

(22) 7,7-Bis(trifluoromethyl)cycloheptatriene exists exclusively as the triene within the limits of detection by nmr spectroscopy: J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965).

(23) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

(24) For an experimental determination of such an interaction see, for instance, G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965).

(25) R. Huisgen, G. Boche, A. Dahmen, and W. Hechte, *Tetrahedron Lett.*, 5215 (1968).

(26) M. J. S. Dewar and N. H. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(27) The influence of the external angle at C-7 on the position of the norcaradiene-cycloheptatriene equilibrium is demonstrated by the observation¹⁸ that Diels-Alder adducts to the cyclopentadiene ring of **16** exist in the cycloheptatriene form. Cf. also M. Jones, Jr. and E. W. Peirillo, Jr., *Tetrahedron Lett.*, 3953 (1969); C. J. Rostek and W. M. Jones, *ibid.*, 3957 (1969).

the norcaradienes listed in Table V all have lower entropies than the valence isomeric cycloheptatrienes is not unexpected since the former are much more rigid molecules than the latter.

Finally, the fact that rapid valence isomerization has now been demonstrated for a number of norcaradiene-cycloheptatriene systems makes it almost certain that such equilibria exist in all compounds of this type even though they may as yet escape detection by the methods currently available.

Experimental Section

7-Cyano-7-phenylnorcaradiene (2a). The acetic acid was removed from a sample of 40.4 g of lead tetraacetate by warming to 40° under vacuum. Benzene (1000 ml) and benzoyl cyanide hydrazone²⁸ (6.41 g) were added, and the mixture was stirred at room temperature for 2 hr. Water and Celite were added, the mixture was filtered, and the filtrate was washed with water, 5% sodium bicarbonate solution, and concentrated sodium chloride solution, and dried ($MgSO_4$). The filtered solution of phenyldiazoacetone nitrile was heated under reflux until nitrogen evolution ceased. The solvent was removed and the residue was chromatographed on Florisil. Elution with methylene chloride first gave an unidentified yellow product followed by 7-cyano-7-phenylnorcaradiene. Crystallization of the appropriate fraction from acetonitrile gave 2.71 g (32%) of 7-cyano-7-phenylnorcaradiene (**2a**), mp 137.5–138.5°, unchanged on further crystallization: uv max (cyclohexane) 277 $m\mu$ (ϵ 3100), 270 (3300), 263 (3100), 240 (6900), and 227 (sh, 8700); (MeCN) 276 $m\mu$ (ϵ 2900), 270 (3200), and 240 (6800); ir (KBr) 2230 and 1600 cm^{-1} , among others; nmr ($CDCl_3$) τ 2.6 (narrow multiplet, 5, Ph), 3.4–4.0 (m, 4, H-2,3,4,5), and 6.48 (m, 2, H-1,6). At -71° , the latter signal occurred at τ 6.77, at $+89^\circ$ at τ 6.32.

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.91; H, 5.68; N, 7.35.

Methyl 7-Cyano-7-norcaradienecarboxylate (2b). A solution of methyl cyanodiazooacetate,²⁹ prepared by oxidation of 0.78 g of methyl cyanoglyoxylate hydrazone with 4.1 g of lead tetraacetate in 50 ml of benzene, was irradiated with a Phillips HPK 125 high-pressure mercury lamp through a Pyrex filter for 3 hr. Removal of the solvent and crystallization of the residue from ethanol gave 0.42 g (39%) of methyl 7-cyano-7-norcaradienecarboxylate (**2b**), mp 172–174°, unchanged on recrystallization from ethanol: uv max (cyclohexane) 268 $m\mu$ (ϵ 3200) and 232 (3300); ir max (CCl_4) 1739 cm^{-1} (KBr), 1730 cm^{-1} , among others; nmr ($CDCl_3$) τ 3.0–4.0 (m, 4, H-2,3,4,5), 6.13 (s, 3, COOMe), and 6.75 (m, 2, H-1,6); the spectrum does not change between -70 and $+80^\circ$.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 7.99. Found: C, 68.49; H, 5.22; N, 8.12.

Methyl 7-Phenyl-7-norcaradienecarboxylate (2c). A solution of 3.18 g of methyl phenyldiazoacetate²⁹ in 300 ml of benzene was irradiated at room temperature with a 450-W medium-pressure Hanovia lamp through a Pyrex filter for 2 hr; 0.91 mol equiv of nitrogen was evolved. Removal of the solvent, chromatography of the residue over Florisil, and crystallization of the fraction eluted with benzene from isopropyl alcohol gave 1.25 g (31%) of methyl 7-phenyl-7-norcaradienecarboxylate (**2c**). An analytical sample (isopropyl alcohol) had mp 107–108°; uv max (MeOH) 268 $m\mu$ (ϵ 2500) and 263 (2500); (cyclohexane) 264 (2600) and 260 (sh, 2500); the uv spectrum (in methylcyclohexane) was independent of temperature between -100 and $+90^\circ$; ir max (CCl_4) 3030 (m), 2980 (w), 1743 (s), 1718 (split, s), 1600 (w), 1495 cm^{-1} , among others; (KBr) 3080 (m), 2980 (w), 1711 (s), 1615 (s), 1505 cm^{-1} , among others.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.40; H, 6.12.

Methyl 7-(*p*-Methoxyphenyl)-7-norcaradienecarboxylate (2d). A solution of 0.75 g of methyl *p*-methoxyphenyldiazoacetate²⁹ in 150 ml of benzene was irradiated with a Phillips HPK 125 high-pressure mercury lamp through a Pyrex filter for 3 hr. Removal of the solvent, chromatography of the residue over Florisil, and crystallization of the fraction eluted with benzene from isopropyl alcohol gave 0.16 g (17%) of methyl 7-(*p*-methoxyphenyl)-7-norcaradiene-

(28) A sample of this compound was kindly supplied by Professor H. Shechter and Dr. R. Bernard of Ohio State University.

(29) E. Ciganek, *J. Org. Chem.*, **35**, 862 (1970).

carboxylate (**2d**), mp 133–134°, unchanged on crystallization from isopropyl alcohol; uv max (methylcyclohexane) 286 m μ (ϵ 3300) and 276 (2900), unchanged between -106 and $+90^\circ$; ir max (CCl₄) 1741 and 1717 (split) cm⁻¹, among others; (KBr) 1708 cm⁻¹, among others.

Anal. Calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.41. Found: C, 74.91; H, 6.28.

Methyl 7-(*p*-Nitrophenyl)-7-norcaradienecarboxylate (2e). A solution of 20.33 g of methyl *p*-nitrophenyldiazoacetate²⁹ in 900 ml of benzene was irradiated with a Phillips HPK 125 high-pressure mercury lamp through a Pyrex filter for 12 hr; ca. 1 mol equiv of nitrogen was evolved. Removal of the solvent, chromatography of the residue on Florisil, and crystallization of the fractions eluted with benzene and methylene chloride from 25 ml of isopropyl alcohol gave 14.88 g (60%) of methyl 7-(*p*-nitrophenyl)-7-norcaradienecarboxylate (**2e**), mp 94–95°. Recrystallization from isopropyl alcohol gave an analytical sample: mp 95°; uv max (methylcyclohexane) at -106° , 272 m μ (ϵ 20,000); at $+23^\circ$, 268 m μ (ϵ 15,000); at $+90^\circ$, 265 m μ (ϵ 14,000); (KBr) 274 m μ ; ir max (CCl₄) 1746 and 1726 cm⁻¹, among others, (KBr) 1708 cm⁻¹.

Anal. Calcd for C₁₅H₁₃NO₄: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.62; H, 5.04; N, 4.92.

(Trifluoromethyl)diazoacetone (1f). To a stirred cooled mixture of 5.9 g of lead tetraacetate (free of acetic acid) and 65 ml of anhydrous benzene was added a solution of 1.66 g of trifluoroacetyl cyanide hydrazone³⁰ in 15 ml of benzene. Water (5 ml) and Celite were added after stirring at room temperature for 3 hr and the mixture was filtered. The benzene layer was washed with water and concentrated sodium chloride solution and dried by stirring with magnesium sulfate for 10 min. The filtered solution was filled up to 100.0 ml with benzene.³¹ Triphenylphosphine (2.0 g) was added to a 20-ml aliquot of this solution; after 1 hr at room temperature the solvent was removed and the residue was chromatographed on Florisil. Excess triphenylphosphine was eluted with benzene, followed by 844 mg (88% yield) of trifluoroacetyl cyanide triphenylphosphazene, eluted with THF–methylene chloride (1:1). An analytical sample was prepared by dissolution in 2 ml of methylene chloride, addition of 2 ml of ether, and allowing the mixture to stand at 0° overnight. The pale yellow crystals so obtained (410 mg) melted at 155–158° dec; uv max (MeCN) 307 m μ (ϵ 21,200), 275 (8700), 268 (7300), and 225 (sh 23,900); ir max (KBr) 2205 cm⁻¹, among others.

Anal. Calcd for C₂₁H₁₃F₃N₃P: C, 63.48; H, 3.81; F, 14.35; N, 10.58; P, 7.80. Found: C, 63.62; H, 4.10; F, 14.78; N, 10.74; P, 7.66.

7-Cyano-7-(trifluoromethyl)norcaradiene/7-Cyano-7-(trifluoromethyl)cycloheptatriene (2f \rightleftharpoons 3f). A benzene (1500 ml) solution of (trifluoromethyl)diazoacetone prepared as described above from 9.00 g of trifluoroacetyl cyanide hydrazone and 36.6 g of lead tetraacetate, was stirred under reflux for 16 hr; a total of 1350 ml of nitrogen (84%) was evolved. The solvent was distilled under reduced pressure (160 mm, 60–70° bath temperature); the pale yellow distillate contained 132 mg (1.5%) of the unreacted diazo compound as determined by the amount of trifluoroacetyl cyanide triphenylphosphazene formed on addition of triphenylphosphine.

The residual yellow liquid was shown by gas chromatography (FS-1265 column at 120°, preheater at 135°)³² to be a mixture of unreacted trifluoroacetyl cyanide hydrazone (7%) and two reaction products (6 and 87%, respectively). Distillation through a spinning band column gave a total of 9.76 g in eight fractions: bp 57–76° (7 mm); the early fractions, bp 57–67° (7 mm), contained all the hydrazone in addition to the two products; the 6% product was enriched in the last fractions. The yield of the minor product (2-phenyl-3,3,3-trifluoropropionitrile, **4**) was thus 0.60 g (5%), that of the major product (7-cyano-7-(trifluoromethyl)norcaradiene/7-cyano-7-(trifluoromethyl)cycloheptatriene), 8.46 g (77%); yields based on trifluoroacetyl cyanide hydrazone not recovered with deduction of the 132 mg of unreacted diazo compound isolated). Slow redistillation of the last three fractions (5.69 g) through a spinning band column effected only partial separation of the two products: the boiling point remained at 76° (7.5 mm) throughout the distillation. The first fraction contained 97% 7-cyano-7-

(trifluoromethyl)norcaradiene/7-cyano-7-(trifluoromethyl)cycloheptatriene and 3% 2-phenyl-3,3,3-trifluoropropionitrile; the last fraction was a mixture of 89% of the former and 11% of the latter. Analytical and spectral data of the equilibrium mixture **2f** \rightleftharpoons **3f** were determined on the first fraction: uv max (cyclohexane) 258 m μ (ϵ 3740); (acetonitrile) 259 m μ (3420); ir max (neat) 3075, 2265, 1450, 1430, 1355, 1325, 1305 (vs), 1200 (vs), 1170 (vs), 1090 (vs), 995 (vs), 765 (s), 740 (vs), and 680 cm⁻¹ (vs), among others. The proton and ¹⁹F nmr spectra are given in the Discussion.

Anal. Calcd for C₉H₆F₃N: C, 58.38; H, 3.27; F, 30.79; N, 7.56; mol wt 185. Found: C, 58.40; H, 3.41; F, 31.02; N, 7.72; mol wt (mass spectroscopically), 185.

The 2-phenyl-3,3,3-trifluoropropionitrile (**4**) was isolated by preparative gas chromatography (3.6 m \times 0.9 cm i.d. column packed with 30% FS-1265 on 60–80 mesh firebrick at 128°, preheater at 130°) followed by trap-to-trap distillation. Gas chromatography showed the sample so obtained to contain only about 75% 2-phenyl-3,3,3-trifluoropropionitrile, the remainder probably being α -cyano- β , β -difluorostyrene formed by loss of hydrogen fluoride during the isolation procedure: uv max (cyclohexane) 240 m μ (ϵ 1500), 260 (630), and 267 (350); ir max (neat) 3070, 3040, 2250 (w), 2225 (w), 1700 (m), 1600 (mw), 1550 (m), 1455 (m), 1315 (vs), 1250 (s), 1190 (s), 1130 (s), 1005 (m), 990 (m), 975 (m), 875 (m), 825 (m), 750 (s), and 700 cm⁻¹ (s); mass spectrum: parent at *m/e* 185 (relative abundance 11.4), 165 (5.2), 134 (30), 132 (96), and 130 (100), among others; ¹H nmr (CDCl₃) τ 2.4 (m, 5, Ph) and 5.38 (q, *J* = 7 Hz, 1, CH(CN)CF₃); ¹⁹F nmr (in CDCl₃, shift in hertz from externally substituted Freon 112 at 56.4 MHz) $+90$ (d, *J* = 7 Hz) and additional weak bands at -60 .

Anal. Calcd for C₉H₆F₃N: C, 58.38; H, 3.27. Found: C, 60.31; H, 3.50.

Thermolysis of Methyl 7-Phenyl-7-norcaradienecarboxylate (2c). A degassed solution of 100 mg of methyl 7-phenylnorcaradiene-7-carboxylate and 10 mg of tetramethylsilane in 500 μ l of perdeuteriochloroform was heated at 159 \pm 1° and the sample was analyzed at intervals by nmr spectroscopy. Disappearance of **2c** followed first-order kinetics with *k* = 3.8 \times 10⁻⁶ sec⁻¹; the product formed was methyl diphenylacetate (singlets at τ 2.7, 5.0, and 6.3 in ratio of 10:1:3); no other compounds could be detected in the nmr spectrum.

Thermolysis of methyl 7-(*p*-methoxyphenyl)-7-norcaradienecarboxylate (2d) was carried out as described above. The rate constant at 159 \pm 1° was 5.0 \times 10⁻⁶ sec⁻¹; the product was methyl (*p*-methoxyphenyl)phenylacetate: nmr τ 2.7 (s, 5), 3.2 (AB q, 4), 5.0 (s, 1), 6.2 (s, 3), and 6.3 (s, 3).

Thermolysis of methyl 7-(*p*-nitrophenyl)-7-norcaradienecarboxylate (2e) was carried out as described above. The rate constant at 159 \pm 1° was 3.7 \times 10⁻⁶ sec⁻¹; the product formed was methyl (*p*-nitrophenyl)phenylacetate: nmr τ 2.2 (AB q, 4), 2.7 (s, 5), 4.9 (s, 1), and 6.2 (s, 3).

Thermolysis of methyl 7-cyano-7-norcaradienecarboxylate (2b) was carried out as described above. The half-life at 121 \pm 1° was ca. 9 hr. The product was methyl phenylcyanoacetate, identified by comparison of its infrared spectrum with that of an authentic sample;³³ nmr τ 2.6 (s, 5), 5.2 (s, 1), and 6.2 (s, 3).

Thermolysis of 7-cyano-7-phenylnorcaradiene (2a) was carried out as described above. The half-life at 135° was ca. 8 hr. The products were a ca. 70:30 mixture of diphenylacetoneitrile (nmr τ 2.6 (s, 10) and 4.8 (s, 1)) and compounds having bands at τ 2.5–4.5 and 7.0–7.5 in the ratio of ca. 7:1; the bands at τ 7.0–7.5 consisted mostly of a doublet (*J* = 7 Hz) and another doublet (*J* = 7 Hz) split into doublets (*J* = 1.5 Hz).

Thermolysis of 7-Cyano-7-(trifluoromethyl)norcaradiene/7-Cyano-7-(trifluoromethyl)cycloheptatriene (2f \rightleftharpoons 3f). Samples (50 μ l) of the equilibrium mixture were added to nmr tubes containing 1 ml of CDCl₃ and 60 μ l of cyclohexane. The tubes were sealed after one freeze–thaw cycle and heated in a constant (\pm 0.1°) temperature bath. The disappearance of **2f** \rightleftharpoons **3f** was followed by ¹H nmr spectroscopy by integration of the area under the τ 5.3 peak (1.6-protons) vs. the area of the cyclohexane standard. The concentration of 2-phenyl-3,3,3-trifluoropropionitrile (singlet at τ 2.6) present to the extent of 3% in the sample of **2f** \rightleftharpoons **3f** used, remained constant throughout the thermolysis. The nmr spectrum of the products showed a doublet (*J* = 6 Hz) at τ 2.7 (relative area 3.4), multiplets at 3.1–3.8 (8.0) and 4.2–4.7 (4.9), and a doublet (*J* =

(30) The sample of trifluoroacetyl cyanide hydrazone was kindly supplied by Dr. S. Proskow. Details of its preparation will be published elsewhere.

(31) Isolation of (trifluoromethyl)diazoacetoneitrile was not attempted in view of the probable explosion hazards involved.

(32) Higher temperatures caused new peaks to occur at the expense of the 87% peak.

(33) Prepared by transesterification of ethyl phenylcyanoacetate with methanol and sodium methoxide.

7 Hz) superimposed on a multiplet at 7.2–7.8 (5.1). The spectra after a short period of heating showed the appearance of a triplet ($J = 6$ Hz) τ 6.9 which gradually disappeared on further heating. The disappearance of $2f \rightleftharpoons 3f$ was clearly first order; rate constants at 142.9, 152.0, 159.0, and 168.4° were $1.52 \pm 0.04 \times 10^{-5}$, $3.22 \pm 0.13 \times 10^{-5}$, $6.42 \pm 0.40 \times 10^{-5}$, and $1.27 \pm 0.03 \times 10^{-4} \text{ sec}^{-1}$, respectively. The Arrhenius plot gave $E_a = 30.8 \pm 2.4 \text{ kcal/mol}$ from which were calculated (at 159°) $\Delta H^\ddagger = 30.0 \text{ kcal/mol}$ and $\Delta S^\ddagger = -8.8 \text{ eu}$.

Hydrogenation of 7-cyano-7-(trifluoromethyl)cycloheptatriene/7-cyano-7-(trifluoromethyl)norcaradiene ($2f \rightleftharpoons 3f$) was carried out using palladium on carbon (10%), rhodium on carbon (5%), and prereduced platinum oxide as catalysts in tetrahydrofuran. The ratios of products were determined by gas chromatography (25% XF-1150 silicone oil on 60–80 mesh firebrick at 120°) and by ^{19}F nmr spectroscopy; they are listed in Table IV. The products were isolated by preparative gas chromatography (same column) and purified by trap-to-trap distillation; the order of elution was as listed below.

1-Cyano-1-(trifluoromethyl)cycloheptane (9) showed ^1H nmr (CDCl_3) only absorption at τ 7–9; ^{19}F nmr (CDCl_3 , shift from external Freon 112) +470 Hz (s); ir max (CCl_4) 2910, 2850, 2230 cm^{-1} , among others.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{F}_3\text{N}$: C, 56.53; H, 6.32; mol wt, 191. Found: C, 56.90; H, 6.57; mol wt, 191 (mass spectroscopically).

7-Cyano-7-(trifluoromethyl)norcarane (8) had ^1H nmr (CDCl_3) only absorption at τ 7–9; ^{19}F nmr (CDCl_3 , shift from external Freon 112) +58 Hz (s); ir max (neat) 2920, 2860, 2240, and 1460 cm^{-1} , among others.

Anal. Calcd for $\text{C}_9\text{H}_{10}\text{F}_3\text{N}$: C, 57.14; H, 5.33; F, 30.13; N, 7.40; mol wt, 189. Found: C, 57.00; H, 5.46; F, 29.75; N, 7.49; mol wt, 189 (mass spectroscopically).

2-Cyclohexyl-3,3,3-trifluoropropionitrile (10) had ^1H nmr (CDCl_3) τ 6.73 (q, $J = 8$ Hz of d, $J = 4$ Hz, 1, H-2) and 7.7–9.0 (m, 11, cyclohexyl); ^{19}F nmr (CDCl_3 , shift from external Freon 112) +85 (d, 8 Hz); ir max (neat) 2950, 2880, 2260 cm^{-1} , among others.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{F}_3\text{N}$: C, 56.53; H, 6.32; F, 29.81; N, 7.32; mol wt, 191. Found: C, 56.44; H, 6.46; F, 29.37; N, 7.41; mol wt 191 (mass spectroscopically).

Addition of Cyano(trifluoromethyl)carbene to Cyclohexene. A solution of 0.92 g of trifluoroacetyl cyanide hydrazone³⁰ in 20 ml of distilled 1,2,4-trichlorobenzene was added, over 10 min, with slight cooling, to a stirred mixture of 3.74 g of lead tetraacetate (free of acetic acid) and 60 ml of 1,2,4-trichlorobenzene. After stirring at room temperature for 2 hr, water (15 ml) was added and the layers were separated. The organic layer was washed twice with water and concentrated sodium chloride solution, and dried (magnesium sulfate). The filtered solution was placed in a 300-ml round-bottomed flask connected through a reflux condenser to a trap, cooled with Dry Ice-acetone. Cyclohexane (100 ml) had previously been distilled into this trap. The system was evacuated to 0.2 mm and the solution was stirred at 27° until the yellow color had mostly disappeared. Dry nitrogen was admitted to the trap, the contents of which was refluxed under nitrogen for 24 hr. Removal of the solvent and short-path distillation of the residue gave 0.80 g of a colorless liquid. Gas chromatography (10 ft \times 0.25 in. XF-1150 column at 120°) showed the presence of at least nine components, three of which accounted for 68% of the total. Two of these were shown to be 1,2,4-trichlorobenzene and cyclohexanol. The third major component was collected by gas chromatography; its retention time and infrared spectrum were identical with those of 7-cyano-7-(trifluoromethyl)norcarane obtained by hydrogenation of 7-cyano-7-(trifluoromethyl)cycloheptatriene/7-cyano-7-(trifluoromethyl)norcaradiene.

Hydrogenation of Cycloheptatriene. A solution of 0.42 g of cycloheptatriene (99% purity) in 5 ml of tetrahydrofuran was hydrogenated with 58 mg of rhodium on carbon (5%). A total of 343 ml of hydrogen was taken up at 24° (3.06 mol). The filtered solution was analyzed directly by gas chromatography (10 ft \times 0.25 in. column packed with 25% of 1,2,3-tris(2-cyanoethoxy)propane on 60–80 mesh firebrick at 52°, preheater at 160°); it was then poured into water, and the upper hydrocarbon layer, after washing with water, was also analyzed as described above. Authentic samples of cycloheptane, methylcyclohexane, and norcarane were used as standards. In addition to 99.5% cycloheptane, both analyses showed the presence of a peak (0.5%) having the retention time of methylcyclohexane; this may have been formed from the toluene present in the cycloheptatriene used. Norcarane was absent within the limits of detectability (estimated at 0.005%).

Hydrogenation of 7-Cyanocycloheptatriene. Catalytic hydrogenation of a solution of 0.39 g of 7-cyanocycloheptatriene in 8 ml of tetrahydrofuran with 97 mg of palladium on carbon (10%) resulted in the uptake of 248 ml of hydrogen at 25° (3.04 mol). Removal of the solvent gave 0.38 g of a colorless oil which on short-path distillation (bp ca. 45° (1 mm)) gave 0.35 g (85%) of cyanocycloheptane, n^{20}_D 1.4631. Gas chromatography on two different columns (silicones FS-1265 and XF-1150) showed only one single peak in each case. The infrared spectrum was identical with that of the sample prepared from bromocycloheptane (see below).

Cyanocycloheptane. A mixture of 24.5 g of bromocycloheptane, 14.0 g of sodium cyanide, 10 g of sodium iodide, and 125 ml of 80% ethanol was stirred under reflux for 20 hr. The cooled, filtered mixture was poured into 800 ml of water and extracted repeatedly with methylene chloride. The combined, washed, and dried extracts were concentrated. A band at 2150 cm^{-1} in the infrared spectrum of the residue pointed to the presence of cycloheptyl isocyanide. Distillation through a spinning band column gave 6.33 g of a mixture in six fractions, bp 74–109° (22 mm). Gas chromatography (XF-1150 column at 146°) showed the presence of four components in the amounts of 24, 14, 3, and 59% (in the order of the boiling points). The 59% component was cyanocycloheptane (22% yield); the others probably were bromo- and iodocycloheptane and cycloheptyl isocyanide. Analytical and spectral data were obtained on the last fraction, bp 109° (22 mm), n^{24}_D 1.4625 (lit.³⁴ bp 85–86° (10 mm), n^{20}_D 1.4655), which was 97.5% cyanocycloheptane: ir max (neat) 2250 cm^{-1} , among others; there was only end absorption in the uv spectrum.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{N}$: C, 77.99; H, 10.63; N, 11.37. Found: C, 78.33; H, 10.66; N, 11.46.

Hydrogenation of ethyl 7-cycloheptatrienecarboxylate was carried out using palladium on carbon (10%), prereduced platinum oxide, and rhodium on carbon (5%) as catalysts and tetrahydrofuran as solvent. Uptake of hydrogen at 25° was 2.84, 2.68, and 2.79 mol equiv, respectively. Removal of the solvent and short-path distillation of the residue gave the hydrogenation products in 93, 95, and 95% yields, respectively. Gas chromatographic analyses (10 ft \times 0.25 in. column packed with silicone XF 1150 at 150°) were carried out before and after distillation. The ratios of products are listed in Table IV. The products were isolated by preparative gas chromatography (3.6 m \times 0.9 cm column packed with 25% of silicone XF-1150 on 60–80 mesh firebrick at 150°) and identified by their infrared spectra.

Ethyl Cycloheptanecarboxylate. A mixture of 1.22 g of cyanocycloheptane (see above), 25 ml of 95% ethanol, and 1.95 g of concentrated sulfuric acid was stirred under reflux for 5 hr. The mixture was poured into water and extracted with methylene chloride, and the extracts were washed with potassium carbonate solution and water, and dried. Removal of the solvent and short-path distillation of the residue gave 0.23 g (14%) of ethyl cycloheptanecarboxylate: bp ca. 45° (0.7 mm), n^{24}_D 1.4507 (lit.³⁵ bp 74° (3 mm), n^{20}_D 1.4487).

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.54; H, 10.65. Found: C, 70.49; H, 10.62.

Ethyl Cyclohexylacetate. A mixture of 73.0 g of cyclohexylacetic acid, 230 g of anhydrous ethanol, 150 ml of dichloroethane, and 2 ml of concentrated sulfuric acid was heated under reflux for 16 hr. Isolation as described for ethyl cycloheptanecarboxylate gave 74.1 g (86%) of ethyl cyclohexylacetate, bp 107–108° (22 mm), n^{24}_D 1.4426 (lit.³⁶ bp 98–100° (17 mm)).

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.54; H, 10.65. Found: C, 70.32; H, 10.51.

Ethyl *exo*- and *endo*-7-Norcaranecarboxylate.^{7,37} To a vigorously stirred mixture of 100 ml of cyclohexene and 5.0 g of copper powder, maintained at 90°, was added, over 7 hr, a solution of 42.6 g of ethyl diazoacetate in 45 ml of ether. After refluxing for a further 30 min, the filtered solution was concentrated and the residue was distilled slowly through a spinning band column. Nine fractions with a total of 26.27 g of product, bp 114–123° (22 mm), were collected. Gas chromatography (silicone XF 1150 column at 135°) before distillation showed the presence of ethyl *exo*-7-norcaranecarboxylate (77%, 32% yield), ethyl *endo*-7-norcaranecarboxylate (7%, 3% yield), diethyl fumarate (6%, 5% yield), and diethyl

(34) E. Müller and H. Huber, *Chem. Ber.*, **96**, 670 (1963).

(35) V. P. Gol'mov, *Zh. Obshch. Khim.*, **23**, 991 (1963).

(36) M. G. Darzens, *C. R. Acad. Sci., Paris*, **144**, 330 (1907).

(37) F. Ebel, R. Brunner, and P. Mangelli, *Helv. Chim. Acta*, **12**, 19 (1929).

maleate (10%, 8% yield). The last two fractions were essentially pure exo ester, bp 123° (22 mm), n_D^{20} 1.4675 (lit.³⁷ bp 109–110° (18 mm)).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 71.39; H, 9.59. Found: C, 71.41; H, 9.62.

The endo ester was isolated by gas chromatography and purified by short-path distillation.

Anal. Calcd for $C_{10}H_{16}N_2$: C, 71.39; H, 9.59. Found: C, 71.39; H, 9.74.

The infrared spectrum of the endo ester is very similar to that of the exo isomer with slight differences in the fingerprint region. Thus, a single band at 950 cm^{-1} in the endo isomer is split into a doublet in the exo compound; a band at 840 cm^{-1} , present in the exo isomer, is absent in the endo isomer, which in turn shows a band at 815 cm^{-1} , absent in the exo isomer. The two isomers, however, are well separated by gas chromatography on a silicone XF-1150 column at 135°; relative retention times: endo, 15.9 min; exo, 20.9 min.

Inert Carbon Free Radicals. I. Perchlorodiphenylmethyl and Perchlorotriphenylmethyl Radical Series^{1,2}

Manuel Ballester,* Juan Riera, Juan Castañer, Carlos Badía, and José M. Monsó

Contribution from the Instituto de Química, Centro de Investigación y Desarrollo, Patronato "Juan de la Cierva," Zona Universitaria, Barcelona 17, Spain.

Received April 17, 1970

Abstract: A number of extremely stable chlorocarbon free radicals derived from diphenylmethyl and triphenylmethyl are here described and examined. They are obtained either by dechlorination of alkaromatic chlorocarbons or oxidation of the corresponding perchlorocarbanions. Perchlorodiphenylmethyl (PDM), perchloro-4-phenyldiphenylmethyl (PPDM), perchloro-4,4'-diphenyldiphenylmethyl (PDDM), perchlorotriphenylmethyl (PTM), perchloro-4-phenyltriphenylmethyl (PPTM), perchloro-4,4'-diphenyltriphenylmethyl (PDTM), and perchloro-4,4',4''-triphenyltriphenylmethyl (PTTM) have been obtained. Perchloro- α,α',α'' -tetraphenylbi-*p*-tolyl- α,α' -ylene (PTBT), a biradical, has also been synthesized. Some of these radicals (PTM series) have in the air half-lives of decades, and withstand typical radical reagents (nitric oxide, hydroquinone, quinone) and even highly aggressive chemical species (concentrated sulfuric and nitric acids, sodium hydroxide, halogens) with little or no alteration. Also, they possess a remarkably high thermal stability (up to 300°). They are all completely disassociated both in solid form and in solution. The epr, uv-visible, and ir spectra of these radicals and related quasi-perchloro compounds are examined. Application of Ballester, Riera, and Spialter spectral correlation for benzene derivatives shows that in these radicals the band found in the vicinity of 300 nm corresponds to the 1L_b electronic transition (secondary band). Evidence is presented showing the steric nature of these radicals' inertness. The synthesis of a number of related new compounds is here described.

Since Gomberg reported in 1900 the detection of the first free radical a great number of stable radicals have been detected and even isolated.³

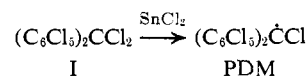
The carbon free radicals are highly reactive species. Nevertheless, some of them show a remarkable stability, the best example being, possibly, Kuhn's 2-(*p*-biphenyl)bisbiphenylallyl⁴ that in solution has a half-life of 10 hr, does not react under mild conditions with some typical radical traps (hydroquinone or iodine), and withstands temperatures close to 100°.

Thermal and chemical stabilities of free radicals are governed by two main factors: resonance and steric hindrance.³ Since the alkaromatic chlorocarbons show great steric effects (inhibition of resonance, shielding, strain, and distortion),^{5,6} which frequently cause high thermal stability and chemical inertness,⁷ it seemed

promising to attempt the synthesis of certain alkaromatic chlorocarbon free radicals.

Evidence for the simplest radical of this type—the perchlorobenzyl radical—was reported by Ballester and coworkers in the chemistry of perchlorotoluene (reaction with iodide⁸ or stannous ions,⁹ pyrolysis,¹⁰ photolysis¹¹).

The preparation—although in a very low yield—of perchlorodiphenylmethane (I) by perchlorination of benzophenone chloride with reagent BMC^{12,13} allowed, under conditions similar to those leading to the formation of transient perchlorobenzyl, the synthesis of radical perchlorodiphenylmethyl (PDM).¹⁴



(1) This research has been sponsored by the Aerospace Research Laboratories (Wright-Patterson A. F. B., Ohio) through the European Office of Aerospace Research, under Contract AF 61 (052)-749.

(2) Some results here reported have been presented before the IUPAC Symposium on "Free Radicals in Solution" (Gomberg Symposium), University of Michigan, Ann Arbor, Mich., Aug 1966.

(3) M. Ballester, *Pure Appl. Chem.*, **15**, 123 (1967).

(4) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

(5) M. Ballester, *Bull. Soc. Chim. Fr.*, **7** (1966).

(6) M. Ballester, *et al.*, "The Chlorocarbons. Anthology I," L. Spialter, Ed., Aerospace Research Laboratories (USAF), ARL-67-0167, 1967.

(7) M. Ballester, J. Castañer, and J. Riera, *J. Amer. Chem. Soc.*, **88**, 957 (1966).

(8) M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).

(9) J. Riera-Figueras, Doctoral Thesis, Universidad de Barcelona, April 12, 1962.

(10) M. Ballester, C. Molinet, and J. Rosa, *An. Real. Soc. Espan. Fis. Quim., Ser. B*, **57**, 393 (1961).

(11) M. Ballester and J. Castañer, *ibid.*, *Ser. B*, **62**, 397 (1966).

(12) M. Ballester, C. Molinet, and J. Castañer, *J. Amer. Chem. Soc.*, **82**, 4254 (1960).

(13) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1131.

(14) M. Ballester and J. Riera, *J. Amer. Chem. Soc.*, **86**, 4505 (1964), preliminary communication.