

anhydrous¹⁹ formic acid for 18 min. at 24°. The red solution was then added slowly with stirring to a mixture of 77 ml. of 50% sodium hydroxide solution and 150 g. of ice. After the addition was complete, the mixture was saturated with sodium chloride, stirred for 2 hr. at 24°, and extracted thoroughly with ether. The organic layers were washed with saturated brine and dried over anhydrous sodium sulfate. The residue obtained on evaporation of the ether by distillation through a 24-in. Podbielniak column was diluted with 10 ml. of carbon disulfide and a portion was submitted to vapor phase chromatography through a preparative Craig succinate column at 190°. The fraction corresponding to the major peak (see above) was collected. The n.m.r. spectrum of this fraction (CDCl₃ solution) showed absorption for 2 protons as a multiplet centered at δ 5.55 p.p.m. (vinylic protons), 1 proton as a broad multiplet at 3.2–3.8 p.p.m., 1 proton as a singlet at 2.67 p.p.m. (–OH), and 12 protons at 1.0–2.3 p.p.m. (CH and CH₂). A 67-mg. sample of this octalol fraction was dissolved in 5 ml. of acetone and titrated with Jones reagent²² at 0° until the color of the reagent persisted. The mixture was

then stirred for 10 min. at 0°, then diluted with 10 ml. of saturated brine, and extracted with ether. The ether layers were washed with saturated brine and dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the ether amounted to 59 mg. of a colorless oil, $\lambda_{\text{max}}^{\text{film}}$ 5.83 μ (C=O). The 2,4-dinitrophenylhydrazone was obtained from ethanol-ethyl acetate as yellow plates, m.p. 167–168°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 367 m μ (ϵ 25,410).

Anal. Calcd. for C₁₆H₁₈O₄N₄: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.0; H, 5.65; N, 16.9.

The n.m.r. spectrum of the 2,4-dinitrophenylhydrazone in CDCl₃ solution exhibited absorption for 2 protons as a singlet at δ 5.65 p.p.m. (vinylic protons).

Acknowledgment.—We are grateful to Dr. L. J. Durham for performing the quantitative n.m.r. spectroscopic analyses. We also wish to thank the U. S. Public Health Service and the National Science Foundation for assisting this study.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF., AND THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Thermal Rearrangements of the 7-Carbomethoxy- Δ^2 -norcarenes¹

By JEROME A. BERSON² AND ELLI S. HAND

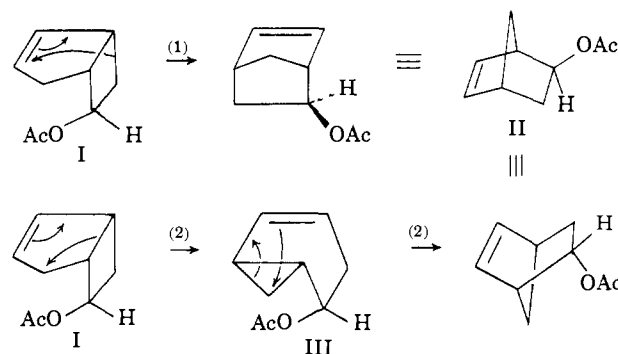
RECEIVED DECEMBER 23, 1963

Pyrolysis of the epimeric esters of the title compound at 425° leads to three sets of products: (i) dihydrophenylacetic ester derivatives and the corresponding aromatic; (ii) cyclopentadienecarboxylic ester and ethylene; (iii) *o*- and *p*-toluic esters and their dihydro analogs (but no *m*-toluic ester). The most likely mechanisms for these processes are, respectively: (i) C₁–C₇ cleavage to a diradical; (ii) vinylcyclopropane rearrangement followed by fragmentation; (iii) a new type of cleavage, leading to an open-chain heptatrienecarboxylic ester, followed by hydrogen shifts and cyclizations. The latter cleavage of the bicyclo[4.1.0]heptene-2 system to a 1,4,6-heptatriene is accompanied by at most a trace of the type of 1,5-hydrogen shift observed by Doering and Grimme in the higher homologs, bicyclo[5.1.0]octene-2 and bicyclo[6.1.0]nonene-2.

In molecular rearrangements that pass over carbonium ion, carbanion, or free radical intermediates, those sites of the reactant at which bonds are broken and new bonds are formed are usually obvious by inspection. Many thermal rearrangements (including some of the so-called "valence isomerizations"), however, are ambiguous in this respect, since the over-all structural change frequently can be formulated as proceeding by way of any of a number of different hypothetical bond reorganization paths. Thus, even the most rudimentary prerequisite for the specification of mechanism is missing. Although it usually is difficult to devise experiments that distinguish cleanly among the various possibilities, the feasibility or likelihood of the proposed component steps can sometimes be tested on independently prepared samples of the hypothetical intermediates or related model substances.

The stereospecific intramolecular thermal isomerization of *syn-cis*-bicyclo[3.2.0]hept-2-enyl-6 acetate (I) to *exo-5*-norbornenyl-2 acetate (II) provides an example of this kind of ambiguity. The rearrangement can be described by at least two paths which have not yet been distinguished from each other.³ One of these is a one-step formal allylic rearrangement of carbon (path 1); the other (path 2) is a two-step process, a preliminary cyclopentene \rightarrow vinylcyclopropane isomerization (I \rightarrow III) followed by conversion

of the intermediate vinylcyclopropane III to a new cyclopentene II. The original object of the present work was to test the feasibility of the hypothetical second step of path 2 by an investigation of the thermal behavior of readily accessible models of III.



For this purpose we prepared *endo*- and *exo*-7-carboethoxy- Δ^2 -norcarenes (IVb and Vb). The action of ethyl diazoacetate on 1,3-cyclohexadiene in the presence of powdered copper^{4,5} gives, in addition to diethyl fumarate and diethyl maleate, at least one 2:1 adduct Vb and the two 1:1 adducts IVb and Vb. Two other 1:1 adducts are formed in minute yields. Saponification and methylation converts these two minor adducts to methyl esters which have vapor chromatographic (v.p.c.) retention times identical with those of au-

(1) This work was supported in part by Public Health Service Grants No. AM06405-01MC and AM07505-01 from the National Institute of Arthritis and Metabolic Diseases.

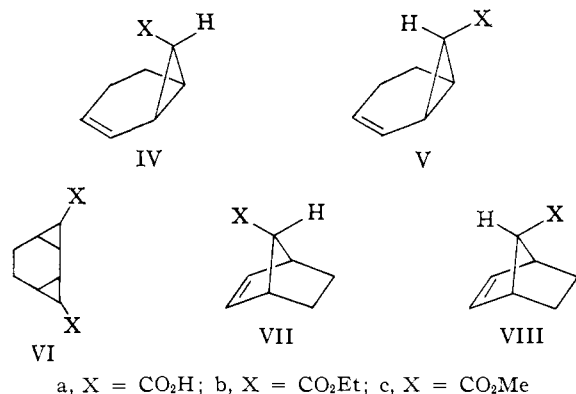
(2) To whom inquiries should be directed at Department of Chemistry, University of Wisconsin, Madison 6, Wis.

(3) J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

(4) P. Besinet, R. Fraisse, R. Jacquier, and P. Viallefont, *Bull. soc. chim. France*, 1377 (1960).

(5) P. C. Guha and G. D. Hazra, *J. Indian Inst. Sci.*, **22A**, 263 (1939); *Chem. Abstr.*, **34**, 2822 (1940).

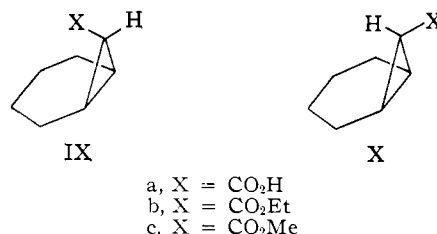
thetic⁶ methyl *syn*- and *anti*-2-norbornene-7-carboxylates (VIc and VIIIc). These products might result from 1,4-addition of a carbenoid fragment to the diene system, a process which while usually subordinate to 1,2-addition is not unprecedented.⁷⁻¹⁰



Analysis by v.p.c. of the reaction mixture shows that the two 1:1 adducts IVb and Vb are formed in the ratio of about 1:5. It seems likely that the predominant isomer is the *exo* compound Vb. Saponification of the mixture of IVb and Vb with aqueous alkali probably does not cause much epimerization, since the firmly identified (see below) *endo*-methyl ester IVc is only slowly epimerized in base. From the resulting mixture of acids, *exo*-acid Va is separated in 67% yield by direct crystallization. Its properties agree with those of the acid Va previously assigned⁴ the *exo* configuration. An additional quantity of Va is obtained, as well as some of the *endo*-acid IVa, by processing the noncrystalline residue by the iodolactone procedure.⁴ Treatment of the iodolactone with zinc gives the previously undescribed *endo*-acid IVa.

Diazomethane converts the two acids to their respective methyl esters. The stereochemical assignments follow from the preparation of the *endo*-acid IVa from the iodolactone and from the observation that the *endo*-methyl ester IVc is slowly epimerized by sodium methoxide in boiling methanol to a mixture of two parts of Vc and one of IVc. It is not clear that this ratio represents equilibrium, but the experiment suffices to demonstrate that the ester prepared from acid that does not form an iodolactone is the more stable one. Finally, the *endo*-acid IVa upon hydrogenation gives a 7-norcaranecarboxylic acid of m.p. 79–80°, whereas the *exo*-acid Va gives an epimeric 7-norcaranecarboxylic acid of m.p. 95–96.5°. These properties are in accord with those reported^{11,12} for the *endo*(IX) and *exo*(X)-7-norcaranecarboxylic acids, respectively.

Although the method of preparation, the physical properties, and the chemical behavior outlined above all point to the *endo* configuration and the 7-carbomethoxy- Δ^2 -norcarenene structure IV for the series of



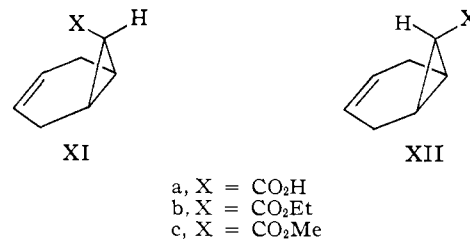
compounds derived from the minor 1,3-cyclohexadiene-diazoacetic ester adduct, a disturbing anomaly comes to light in the nuclear magnetic resonance (n.m.r.) spectrum. The data for the methyl ester we assign structure IVc are shown in Table I along with those for

TABLE I
PROTON MAGNETIC RESONANCE SPECTRA^a

	Vinyl H	CO ₂ CH ₃	CH ₂	Cyclopropyl H
<i>endo</i> - Δ^2 -IVc	5.70 (2)	3.56 (3)	2.02 (4)	1.66 (3)
<i>exo</i> - Δ^2 -Vc	5.96 (1), 5.48 (1)	3.58 (3)	1.84 (7)	
<i>endo</i> - Δ^3 -XIc	5.49 (2)	3.56 (3)	2.31 (4)	1.50 (3)
<i>exo</i> - Δ^3 -XIIc	5.50 (2)	3.61 (3)	2.40 (4)	1.62 (3)

^a The spectra of carbon tetrachloride solutions were taken with the Varian A-60 spectrometer. Chemical shifts are given in p.p.m. relative to tetramethylsilane as internal reference. Only the carbomethoxy proton signals appear as sharp singlets; the other bands are poorly resolved multiplets, the positions of which are indicated in the table as approximate centers of gravity. The numbers in parentheses refer to approximate relative areas.

the *exo* epimer Vc. Whereas the latter compound shows two clearly separated regions of vinyl proton absorption, the *endo* compound IVc shows only one, suggesting that it might have a symmetrical structure with chemically identical vinyl protons. The only other structure that would fit the properties of the substance we call IVc would be *endo*-7-carbomethoxy- Δ^3 -norcarenene (XIc). Formation of a Δ^3 -norcarenene



from 1,3-cyclohexadiene would require a double bond migration. This reaction seems inherently improbable, especially since it would be necessary to assume its occurrence in the formation of only one of the two products XIb and XIIb allegedly resulting from the reaction with diazoacetic ester. Further, it would be necessary that the sodium methoxide-catalyzed interconversion of the two methyl esters previously formulated as an epimerization (IVc \rightarrow Vc) now include a double bond shift (XIc \rightarrow Vc). Even this remote possibility is excluded by the preparation of the authentic 7-carbomethoxy- Δ^3 -norcarenene (XIc and XIIc). The mixture of ethyl esters XIb and XIIb resulting from the reaction of 1,4-cyclohexadiene and ethyl diazoacetate gives two crystalline acids upon saponification. The *exo*-acid XIIa, which does not form an iodolactone, gives *exo*-7-norcaranecarboxylic acid (Xa) upon hydrogenation; the *endo*-acid, regenerated from its iodolactone, gave the *endo* isomer IXa. These new acids (XIa and XIIa) from 1,4-cyclohexadiene,

(6) R. R. Sauers, *Chem. Ind.* (London), 176 (1960). We are indebted to Dr. Sauers for kindly supplying samples of these materials and their nuclear magnetic resonance and infrared spectra.

(7) W. von E. Doering and D. E. MacDuffie, unpublished; D. E. MacDuffie, Dissertation, Yale University, 1959.

(8) V. Franzen, *Chem. Ber.*, **95**, 571 (1962).

(9) B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3826 (1962).

(10) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962).

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

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

and the corresponding methyl esters XIc and XIIc, are clearly different from their counterparts obtained from 1,3-cyclohexadiene. There can be little question, therefore, that the products from 1,4-cyclohexadiene belong to the Δ^3 -norcarene series and those from 1,3-cyclohexadiene belong to the Δ^2 -norcarene series. The n.m.r. spectra of the Δ^3 -methyl esters XIc and XIIc, shown in Table I, are compatible with a symmetrical environment for the double bond, the vinyl proton region showing only a single poorly resolved multiplet. We are forced to the conclusion that the apparent single absorption in this region for the unsymmetrical *endo*-ester IVc results from a fortuitous near-correspondence of chemical shifts for the two vinyl protons.

Stereochemistry of the Pyrolyses of the 7-Carbomethoxy- Δ^2 -norcarenes.—In the conversion of a Δ^2 -norcarene to a 2-norbornene intended to serve as a model for the hypothetical III \rightarrow II reaction of path 2, the presence of a 7-substituent on the Δ^2 -norcarene potentially might provide a means of gaining some additional mechanistic insight, since it might allow an inspection of the stereochemical relationship at C-7 of starting material and product, the site of the key bond-reorganization process. However, this aim is frustrated because the *endo*- and *exo*-7-carbomethoxy- Δ^2 -norcarenes (IVc and Vc) do not follow independent paths of pyrolysis; the *endo* ester IVc is almost quantitatively converted to the *exo* isomer Vc at 300° at a rate much faster than either one is converted to rearrangement products. The *exo* isomer also forms a small amount of *endo* on pyrolysis. The pyrolyses of the isomers then are inseparable in practice, and accordingly we report on only the more readily accessible *exo* isomer Vc in detail.

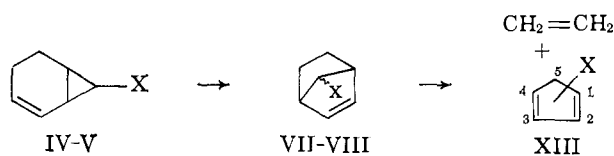
The mechanism of the *endo* \rightarrow *exo* conversion, which is a formal epimerization, is not entirely clear. It could conceivably result from a heterogeneously catalyzed enolization at a glass surface, but a plausible alternative is the homogeneous, purely thermal type of stereochemical isomerization observed in the conversion of *cis*-1,2-dideuteriocyclopropane to the *trans* isomer,¹³ a reaction that probably involves^{13,14} cleavage of the doubly allylic bond (see below) to a diradical, rotation, and recyclization. Conceivably the epimerization could be suppressed by the use of a saturated C-7 substituent instead of carbomethoxy.

Pyrolysis of *exo*-7-Carbomethoxy- Δ^2 -norcarene (Vc).—Although the *exo* ester Vc decomposes at 300–350°, the reaction is inconveniently slow, and most of our results pertain to pyrolyses carried out in the gas phase at a reaction temperature of 425°. Although recycling is necessary to achieve high conversions, most of the products formed at low temperature and in single passes seem to be the same as under the more vigorous conditions. Vapor chromatographic analysis of the crude liquid product indicates the presence of at least twenty-three components. The complexity of this forbidding mixture is substantially reduced by catalytic hydrogenation, which gives a product showing only twelve peaks of intensity more than 2% of the total in the v.p.c. This suggests the presence in the original pyrolysis product of groups of substances of identical

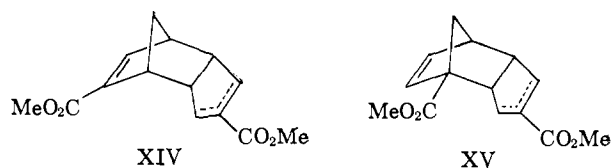
carbon skeleton but differing oxidation state. The conditions of the hydrogenation are such that aromatics survive, and their presence is evident from ultraviolet and infrared spectra. Even without regard to detailed structure, the formation of benzene derivatives from a norcarene represents net dehydrogenation, a process that is familiar in the high-temperature chemistry of hydroaromatics.¹⁵

Among the minor products (identified by v.p.c. retention times and/or ultraviolet spectra only) are cyclohexene, benzene, and toluene. These represent the occurrence of degradative processes that are relatively slow at these temperatures.¹⁵

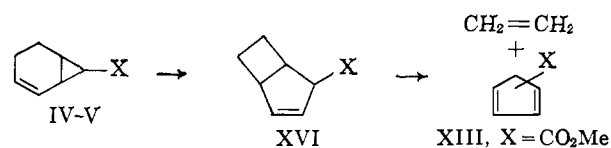
A major gaseous product is ethylene, identified by v.p.c. and by conversion to and isolation of ethylene bromide. The source of this product may be in the Diels–Alder retrogression of the 7-carbomethoxy-2-norbornenes (VIIc and VIIIc) we originally had hoped to observe as products from a rearrangement (IV–V \rightarrow VII–VIII) analogous to step 2 (III \rightarrow II) of path 2. In accord with this origin for the ethylene, a substantial



quantity of carbomethoxycyclopentadiene XIII is present in the liquid product. This material has a v.p.c. retention time identical with that of the substance assigned¹⁶ the structure 1-carbomethoxycyclopentadiene. Although our product XIII might conceivably be a mixture or a double bond isomer, the question is without mechanistic significance, since rapid thermal isomerizations of the double bonds would be likely to occur (see below) in the anticipated proximate product, 5-carbomethoxycyclopentadiene, of the Diels–Alder retrogression of VIIc–VIIIc. Product XIII is present only in fresh pyrolysate from Vc. When aged, these preparations give the two known Diels–Alder dimers XIV and XV^{16b} of XIII.



The formation of ethylene and methyl cyclopentadienecarboxylate XIII is consistent with the anticipated rearrangement IV–V \rightarrow VII–VIII, *i.e.*, Δ^2 -norcarene \rightarrow 2-norbornene, or with an alternative path, the norcarene \rightarrow bicyclo[3.2.0]heptene rearrangement IV–V \rightarrow XVI, followed by cleavage of XVI. These alternatives are analogous to the hypothetical connection of III to



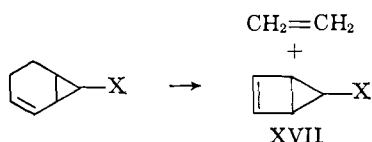
(15) J. Shabtai and E. Gil-Av, *Tetrahedron*, **18**, 87 (1962), and references cited therein.

(13) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(14) S. W. Benson, *ibid.*, **34**, 521 (1961).

(16) (a) K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Chem. Ber.*, **87**, 1752 (1954); (b) D. Peters, *J. Chem. Soc.*, 1761 (1959), and references therein cited.

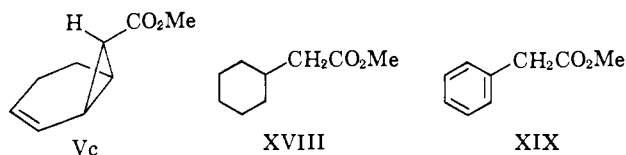
both I and II in path 2 above. As a third formal, but less likely, alternative there is the possibility of a direct fragmentation. The bicyclo[2.1.0]pentene XV-



II would be expected to isomerize readily to XIII at these temperatures.

In the Experimental section are described the details of an assiduous search of the pyrolysate for the 7-carbomethoxynorbornenes VIIc and VIIIc. If present at all, these materials constitute at most 0.5% of the product, even from pyrolysates obtained at lower temperatures and in single passes. Material from the only peak in the v.p.c. spectrum that could represent one of these (VIIIc) can be isolated preparatively but has an infrared spectrum entirely different from that of VIIIc. The failure to find VIIc and VIIIc is not surprising, since even had they been authentic products of the pyrolysis, they would have been expected to suffer Diels-Alder retrogression at least partially if not completely. Although VIIc and/or VIIIc are likely sources of ethylene and methyl cyclopentadienecarboxylate in the pyrolysis, there is presently no direct evidence favoring this origin over the other two possibilities.

The three-membered ring of the starting *anti*- Δ^2 -norcarene ester Vc cleaves in another mode that leads to the cyclohexylacetic ester skeleton. Methyl cyclohexanecarboxylate (XVIII) and methyl phenylacetate

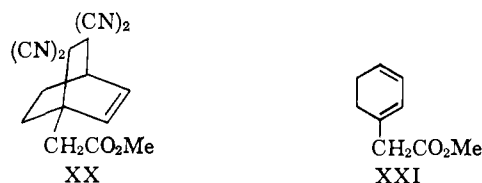


(XIX) constitute a substantial fraction of the hydrogenated pyrolysate. (Compound XVIII does not arise from hydrogenolysis of Vc under the conditions used.) The aromatic substance XIX, having a higher oxidation state than that of the starting material V, presumably arises from over-all disproportionation of the type already mentioned.

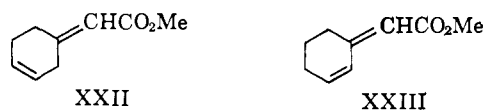
A true isomerization product of Vc with the cyclohexylacetic skeleton is found as a component in one of the fractions from preparative v.p.c. of the pyrolysate. This fraction has a broad ultraviolet absorption maximum at 270 $m\mu$ and reacts with tetracyanoethylene to give a mixture of adducts which has no maxima in the ultraviolet above 210 $m\mu$. One of these adducts is obtained in pure form and is assigned structure XX on the basis of its elemental composition ($\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_2$) and spectral properties, particularly the absence of ultraviolet maxima and the n.m.r. spectrum. The diene precursor of XX is therefore XXI, a structure in accord with the observed 270 $m\mu$ band (calcd.¹⁷ λ_{max} 268 $m\mu$).

Evidence for the presence of a further product having the hydrophenylacetic skeleton is provided by hydrogenation of one of the v.p.c. fractions, which

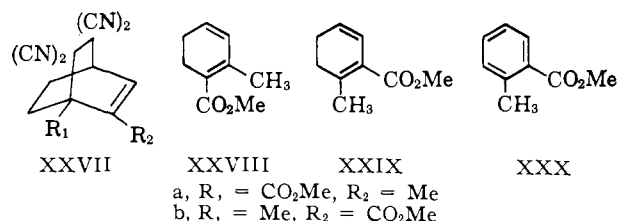
(17) According to the procedure of R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).



gives a mixture containing methyl cyclohexylacetate. The mixture prior to hydrogenation fails to react with tetracyanoethylene and has no high intensity absorption above 250 $m\mu$. Treatment with hot methanolic sodium methoxide causes the appearance of a pronounced ultraviolet absorption band, λ_{max} 264 $m\mu$. This behavior is consistent with and provides circumstantial evidence for the presence in the mixture of the unconjugated dienic ester XXII which would presumably suffer ready isomerization in base to the conjugated structure XXIII. The observed ultraviolet maximum is in good agreement with that expected¹⁸ for this chromophore.



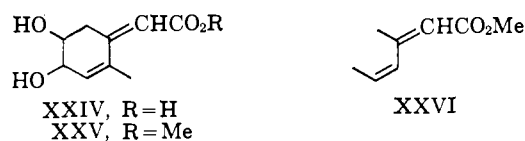
The adduct mixture from the preparation of XX from crude XXI contains a second substance whose n.m.r. spectrum shows a C-methyl singlet. For reasons given in the Experimental, it is likely that this second adduct has structure XXVIIa or XXVIIb and accordingly is derived from one of the dienes XXVIII or XXIX.



More direct evidence for the 2-methylcyclohexanecarboxylic ester type of skeleton is provided by the isolation from the pyrolysate of methyl *o*-toluate (XXX).

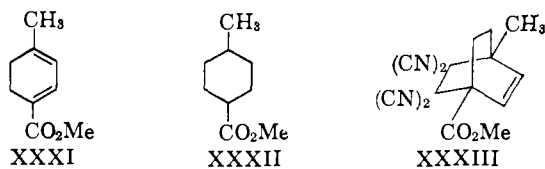
The 4-methylcyclohexanecarboxylic ester skeleton is represented by two pyrolysis products. The first of these, methyl *p*-toluate, is readily identified. The second is assigned the structure 1-carbomethoxy-4-methylcyclohexadiene-1,3 (XXXI) on the basis of its ultraviolet spectrum (λ_{max} 305 $m\mu$; compare 1,6-dicarboxy-4-methylcyclohexadiene-1,3, λ_{max} 296 $m\mu$ ¹⁹); its hydrogenation to a mixture of methyl *cis*- and *trans*-4-methyl-1-cyclohexanecarboxylates (XXXII); and its reaction with tetracyanoethylene to give a crystalline 1:1 adduct XXXIII, which has no ultraviolet

(18) (a) Compare XXIV, λ_{max} 260 $m\mu$ (MeOH); XXV, λ_{max} 267 $m\mu$ (MeOH); R. Grewe and A. Bokrans, *Chem. Ber.*, **88**, 49 (1955); (b) compare XXXVI, λ_{max} 262 $m\mu$ (EtOH); S. Akiyoshi and K. Neno, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 726 (1951).

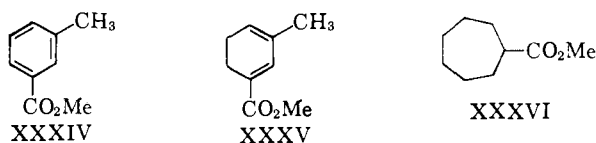


(19) G. F. Hennion, J. J. Sheean, and D. E. Maloney, *J. Am. Chem. Soc.*, **72**, 3452 (1950).

maximum above 210 m μ . The n.m.r. spectrum of the adduct is consistent with the structure XXXIII: It shows two vinyl protons at 6.76 and 6.43 p.p.m., doublets with J 9 c.p.s.; one ester methyl singlet at 4.0 p.p.m.; one C-CH₃ singlet at 1.75 p.p.m.; and four other protons as a complex multiplet extending from 1.4-2.7 p.p.m.



Despite careful searches of the pyrolysate we are unable to find even a trace of methyl *m*-toluate (XXXIV). Control experiments show that methyl *m*-toluate is stable under the pyrolysis conditions. Although evidence on the stability of the hypothetical proximate products with this skeleton (methyl dihydro-*m*-toluates, e.g., XXXV) is lacking, it is reasonable to suppose that since the products of this oxidation state and the fully aromatic counterparts are found in both the *ortho* and *para* series, the absence of the *meta* aromatic signifies that the dihydro companion never is formed.



The relative proportions of the eight major identified products in the nongaseous fraction of the pyrolysate after hydrogenation are shown in Table II. These

TABLE II

RELATIVE PROPORTIONS OF PRODUCTS IN THE NONGASEOUS FRACTION OF THE PYROLYSATE AFTER HYDROGENATION

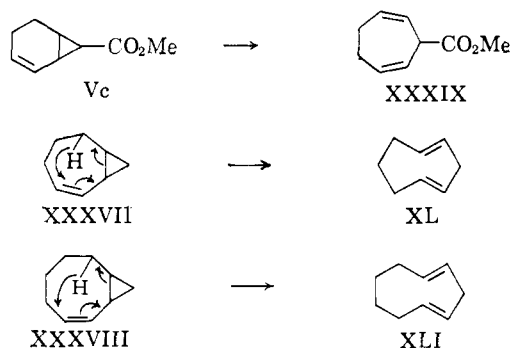
Product, X = CO ₂ Me	Rel. abundance	Product, X = CO ₂ Me	Rel. abundance
	0.63		0.24
	1.12		0.29
	0.98		0.24
	0.34		0.024
			1.00

constitute 80% of this fraction. In addition to these substances, there are five other products, one of which has a v.p.c. retention time identical with that of authentic methyl cycloheptanecarboxylate (XXXVI). The very small amount of this material formed (see Table II) prevents more definite identification, but at least an upper limit can be placed on the yield of XXXVI.

Discussion

The pyrolysis of *exo*-7-carbomethoxy- Δ^2 -norcarene (Vc) differs markedly from those of the two superficially analogous substances bicyclo[5.1.0]octene-2 (XXXVII) and bicyclo[6.1.0]nonene-2 (XXXVIII)

which, like Vc, incorporate a vinylcyclopropane system in a fused ring structure. The over-all 1,5-hydrogen shift accompanied by opening of the cyclopropane ring



shown is the major result of the pyrolyses of XXXVII and XXXVIII, each of which cleanly affords an unconjugated monocyclic diene as product.²⁰ With Vc, the corresponding change would lead to a methyl cycloheptadienecarboxylate XXXIX and hence to the appearance of methylcycloheptanecarboxylate XXXVI in the hydrogenated pyrolysate. The observation that only a trace of this material is formed means that either the reaction Vc \rightarrow XXXIX is an unimportant mode of decomposition or else that the cycloheptadiene ester XXXIX is unstable under the pyrolysis conditions while cyclooctadiene XL and cyclononadiene XLI survive. Although the latter interpretation cannot directly be ruled out in the absence of a control experiment, it seems more likely²¹ that XXXIX is not formed because Vc is consumed more rapidly by other paths.

One of these paths appears to be initiated by cleavage of the C₁-C₇ bond of the norcarene ester Vc. The resulting "diradical" XLII (of unspecified electronic multiplicity) can also be formed from the *endo*-ester IVc, rotation about the C₆-C₇ bond of XLII being free; the reversibility of the IVc or Vc \rightarrow XLII reactions then allows the observed IV \rightleftharpoons V isomerizations.

Intermediate XLII also can be disposed of by 6,1-hydrogen shift to give the unconjugated diene XXII and by 6,7-hydrogen shift to conjugated diene XXI. Evidence for the presence of both XXII and XXI in the pyrolysate has already been given. Regardless of mechanistic details, the reactions Vc \rightarrow XXII and Vc \rightarrow XXI are direct analogs of the well known²⁴

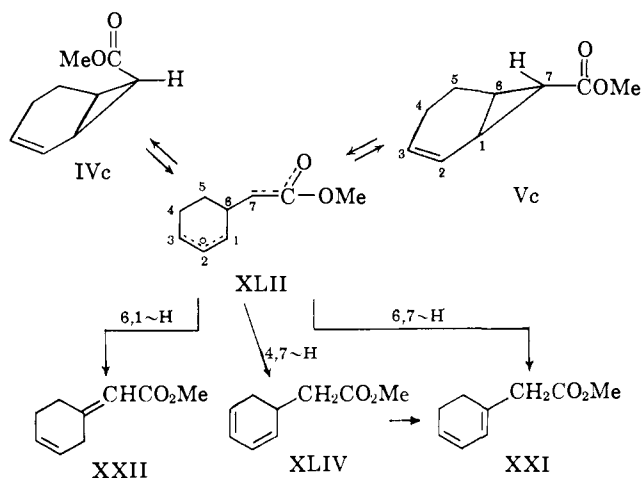
(20) (a) W. von E. Doering and W. Grimme, unpublished observations, cited by W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963). Intrinsically interesting but immaterial in the present context is the fact that the Doering-Grimme rearrangement apparently transfers hydrogen only to the double bond end of the vinylcyclopropane system and not to the cyclopropane end. The latter process would produce a conjugated monocyclic diene, but this type of product from Vc presumably still would give methyl cycloheptanecarboxylate on hydrogenation. For further examples of these rearrangements, see (b) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963); (c) W. R. Roth, personal communication cited in (b).

(21) A major structural difference between a 1,4-cycloheptadiene system such as XXXIX and a 1,4-cycloocta(or nona)diene such as XL or XLI is that the cycloheptadiene is a biallyl and hence subject in principle to the Cope rearrangement. This difference, however, can hardly be the basis of the absence of XXXIX from the pyrolysate, since the hypothetical Cope rearrangement product, a 1,2-divinylcyclopropane-3-carboxylic ester, must surely be unstable with respect to XXXIX. In fact, both *cis*- and *trans*-1,2-divinylcyclopropanes are cleanly isomerized to 1,4-cycloheptadiene.^{22,23}

(22) (a) E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (b) E. Vogel, K.-H. Ott, and K. Gajek, *Ann.*, **644**, 172 (1961); (c) E. Vogel and E. Erb, *Angew. Chem. Intern. Ed. Engl.*, **1**, 53 (1962).

(23) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(24) See ref. 13 and 14 and papers cited therein; see also D. W. Setser



cyclopropane \rightarrow propylene conversion and therefore are in at least a formal sense unexceptional. An alternative route to diene XXI involves 4,7-hydrogen shift in XLII to give the conjugated cyclohexadiene XLIV followed by double bond isomerization of a common type.^{25-28a}

Diradical XLII also represents one way of formulating the vinylcyclopropane rearrangement leading to the 7-carbomethoxy-2-norbornenes which are likely precursors of the observed major products ethylene and methyl cyclopentadienecarboxylate XIII (see above).^{28a} Although the diradical also could lead to a tetrahydrobenzofuran derivative^{28b} by cyclization between C₁ and the carbonyl oxygen, we have no evidence for or against such a product.

An alternative mode of cleavage of the cyclopropane ring involves bond C₁-C₆, which being singly allylic, might be expected to be less easily broken (to give XLV) than the doubly activated C₁-C₇ bond. If such energetic considerations apply to cyclopropane \rightarrow propylene conversions, the almost complete absence of products with the cycloheptane skeleton is quite reasonable. It is conceivable, however, that such products are missing because XLV cyclizes at C₄-C₇ to the bicyclo[3.2.0]heptene derivative XVI which, like 7-carbomethoxy-2-norbornene, would suffer retrogression to ethylene and methyl cyclopentadiene-carboxylate XIII.



Cleavage at C₁-C₆ is the most plausible way of accounting for *o*- and *p*-toluic esters and their dihydro

and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

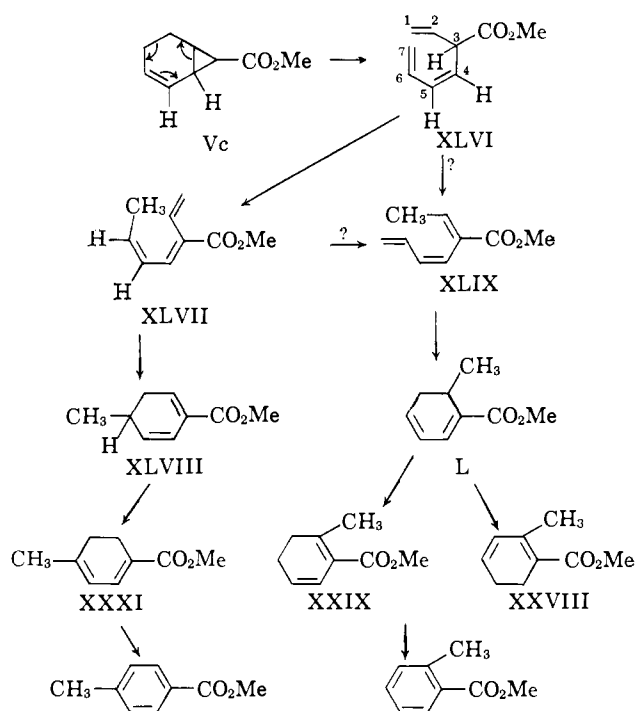
(25) E. D. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

(26) H. Pines and R. H. Kozlowski, *ibid.*, **78**, 3776 (1956).

(27) W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *J. Org. Chem.*, **27**, 1851 (1962).

(28) (a) Although the IVc \rightarrow Vc, Vc \rightarrow XXI, and Vc \rightarrow XXII reactions are readily formulated with the aid of the "diradical" XLII, there is presently no direct evidence that an intermediate is actually involved. Alternative formulations employing only concerted reactions could also be written. Recognizing the difficulties inherent in distinguishing the two kinds of process,²⁴ we emphasize that our choice of one or the other is for the present merely a matter of convenience in notation. (b) *Cf.* formylcyclopropane \rightarrow 2,3-dihydrofuran: C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947); J. Wiemann and S.-L. Thi Thuan, *Bull. soc. chim. France*, 199 (1958).

derivatives XXVIII (or XXIX) and XXXI. A speculative but reasonable mechanism for the formation of these substances is



Opening of Vc in the indicated manner would produce methyl *cis*-1,4,6-heptatriene-3-carboxylate (XLVI), the configuration being the proper one for the subsequent 3,7-hydrogen transfer²⁹ that leads to methyl *cis,cis*-2,4,6-heptatrienecarboxylate (XLVII). Cyclization³⁰ to XLVIII, double bond rearrangement²⁵⁻²⁷ and dehydrogenation¹⁵ follow as unexceptional processes leading to methyl *p*-toluate. The formulation of the processes leading to methyl *o*-toluate and its dihydro derivatives XXIX and XXVIII by way of the conjugated trienes XLVII and XLIX requires either a 1,7-hydrogen transfer or an allylic hydrogen shift, reactions which, so far as we are aware, are unprecedented.³¹⁻³⁵ Nevertheless, even the most plausible alternative seems to be much more objectionable. For example, one might postulate initial rearrangement of Vc to the 7-norbornene derivative VII-VIII, retro-Diels-Alder reaction of the latter to give methyl cyclopentadiene-5-carboxylate (LI) and ethylene, double bond rearrangement³⁶⁻³⁸ to LII, and recombination

(29) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Am. Chem. Soc.*, **84**, 2775 (1962).

(30) *Cf.*, *inter alia*, alloocimene \rightarrow α - and β -pyronenes; L. A. Goldblatt and S. Palkin, *ibid.*, **66**, 655 (1944).

(31) The only cases we know of in which the 1,7-shift has been tested are cyclic ones. With chemically³² or isotopically³³ labeled cycloheptatrienes, 1,5-hydrogen shift appears to be favored over 1,7.

(32) (a) C. Grundmann and G. Ottman, *Ann.*, **582**, 163 (1953); (b) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962).

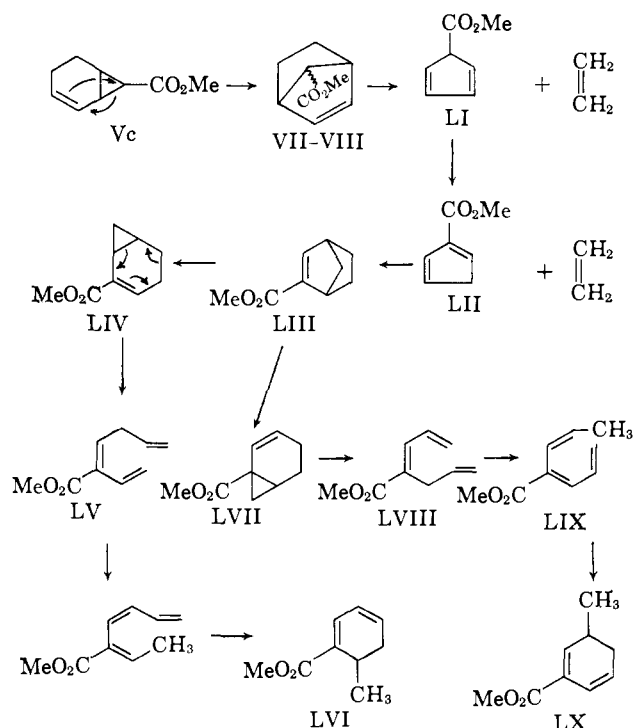
(33) (a) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962); (b) for further examples of 1,5-shift in cases where the 1,7-possibility is not a factor, see ref. 23, and J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963); (c) W. Sanne and O. Schlichting, *Angew. Chem.*, **74**, 156 (1963).

(34) Although the prototropic allylic rearrangement (by ionic processes) is well known and in fact cannot rigorously be ruled out here, we know of no clear example of a purely thermal intramolecular change producing allylic rearrangement of hydrogen. The simplest case examined is that of propylene-1-¹⁴C, which is not converted to propylene-3-¹⁴C at 250°.³⁵

(35) B. Sublett and N. S. Bowman, *J. Org. Chem.*, **26**, 2594 (1961).

(36) That is, hydrogen shift like those of acetoxycyclopentadienes,³⁷ alkylcyclopentadienes,³⁸ and carboalkoxycyclopentadienes.¹⁶

to give 2-carbomethoxynorbornene-2 (LIII). This might be imagined to suffer conversion of the cyclopentene system to a vinylcyclopropane,³⁹ as in LIV. Cleavage of the latter as shown, followed by unexceptional 1,5-hydrogen shift in the product LV and triene cyclization would lead to LVI, a plausible precursor of methyl *o*-toluate and its dihydro derivatives XXVII or XXIX, which are among the products. There are at least two major objections to this mechanism. The first is a general one: Since our pyrolyses of Vc are carried out in the gas phase, intermolecular mechanisms (*cf.* LII \rightarrow LIII) suffer an immediate disadvantage with respect to intramolecular ones, which do not require recombinations. The second



objection is specific: If reaction LIII \rightarrow LIV is assumed, it seems likely that LIII \rightarrow LVII, formation of an alternative vinylcyclopropane, could occur. Application of a series of processes exactly analogous to those postulated for the other vinylcyclopropane LIV would lead ultimately to a derivative of the *m*-toluate system LX. But methyl *m*-toluate is absent from the pyrolysate. Although some special feature of LIII may prevent conversion to LVII (or of LVII to LX), it is not obvious what this might be. The mechanism for formation of LVI by way of LIV thus seems unlikely and, consequently, the preferred formulation at present seems to involve the open-chain trienes XLVI, XLVII, and XLIX. Although perhaps not much of the latter two substances would be expected to survive our pyrolyses (which are carried to

(37) R. B. Woodward and R. Vanelli, unpublished; R. Vanelli, Thesis, Harvard University, 1950, as quoted by M. Rosenblum, *J. Am. Chem. Soc.*, **79**, 3179 (1957).

(38) (a) R. Riemschneider, A. Reisch, and H. Horak, *Monatsh.*, **91**, 805 (1960); (b) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

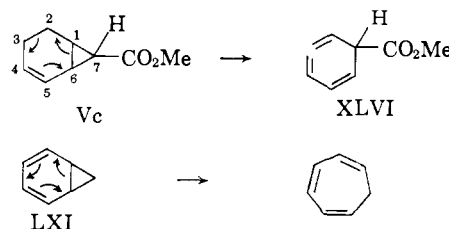
(39) This hypothetical reaction is the analog of that postulated^{23b,40,41} as the first step of the sequence 2,5-norbornadiene \rightarrow norcaradiene \rightarrow cycloheptatriene.

(40) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(41) Whether or not a diradical intermediate⁴⁰ is imagined to intervene need not be specified.

high conversions),⁴² we are able to provide necessary but insufficient evidence from v.p.c. retention times for the presence in the hydrogenated pyrolysate of small amounts of methyl 2-ethylhexanoate, presumably derived from one or more of these acyclic trienes.

The ring opening Vc \rightarrow XLVI is formally the reverse of an intramolecular Diels-Alder reaction. It is also an analog, at the next lower oxidation state, of the norcaradiene \rightarrow tropilidene system,⁴⁴ a σ -bond of Vc playing the role of one of the π -bonds of norcaradiene (LXI). This mode of decomposition obviously is not



available to the bicyclo[5.1.0]octene (XXXVII) or bicyclo[6.1.0]nonene (XXXVIII) systems, where the Doering-Grimme 1,5-hydrogen shifts to give monocyclic dienes predominate.

The major paths of thermal rearrangement of Vc thus seem to be: (a) C₁-C₇ cleavage, leading to methyl phenylacetate and its progenitors; (b) vinylcyclopropane \rightarrow cyclopentene rearrangement, leading ultimately to carbomethoxycyclopentadiene and ethylene; and (c) decyclization leading ultimately to products derived from an open-chain triene.

Experimental⁴⁵

Reaction of Cyclohexadiene-1,3 with Ethyl Diazoacetate.^{4,6-} To a boiling mixture of 15.6 g. of cyclohexadiene-1,3,⁴⁶ 0.2 g. of powdered copper, and about 2 ml. of ethyl diazoacetate⁴⁷ was added dropwise under reflux during 40 min. the remainder of the ethyl diazoacetate charge (total 24.5 g.). After having been heated at reflux an additional 15 min., the reaction mixture was no longer evolving gas. It was cooled, diluted with ether, combined with another batch (prepared under the same conditions from 10.0 g. of cyclohexadiene-1,3 and proportionate quantities of other reagents), filtered, and distilled under nitrogen through a Vigreux column. After a low-boiling forerun had been discarded, fraction A, 29.0 g. of material boiling in the range 72 (30 mm.) to 95° (1 mm.), was collected. This consisted of about 5% diethyl

(42) Neglecting any resonance energy differences (which probably are small) and entropy differences, a linear conjugated triene is unstable (at about room temperature) with respect to the corresponding cyclohexadiene by just the difference in strength between the two links of a carbon-carbon double bond (*ca.* 20 kcal./mole⁴³). Given the repeated chances to cyclize provided by our conditions, it is likely that most of the XLVII and/or XLIX formed would have been converted to cyclohexadienes and products derived from them.

(43) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co., Ltd., London, 1958, p. 273.

(44) *Cf.* W. von E. Doering and M. R. Willcott, *Tetrahedron Letters*, 663 (1962), and references therein cited.

(45) Melting points and boiling points are uncorrected. Infrared spectra of solids (as mineral oil mulls) and of liquids (neat) were taken with a Perkin-Elmer Infracord spectrometer. A few of the vapor chromatographic analyses were performed with a Carbowax 400 6 ft. \times 0.25 in. column on the Perkin-Elmer Model 154C instrument with helium carrier, but most of the work was done with a Barber-Colman Model 20 instrument using capillary columns coated with either tricyanoethoxypropane (TCEP) or Ucon 50HB-2000 (Union Carbide Corp.) in lengths of 150 and 100 ft., respectively, at 125° and 45 p.s.i. with argon carrier. Preparative vapor chromatographic separations were carried out with a 10 ft. \times 1/8 in. phenyl-diethanolamine succinate (PDEAS) column at 150° and 200 ml./min. helium flow using the Wilkens Aerograph A-700 Autoprep instrument. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by Mr. Joseph F. Alicino, Metuchen, N. J.

(46) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(47) *Org. Syntheses*, **36**, 25 (1956).

fumarate, 9% diethyl maleate, and 14 and 72%, respectively, of *endo*- and *exo*-7-carboethoxybicyclo[4.1.0]heptene-2 (7-carboethoxy- Δ^2 -norcarenes, IVb and Vb). The dark brown residue (21 g.) could not be distilled or crystallized. It was saponified by boiling in a mixture of 200 ml. of 10% aqueous sodium hydroxide and 150 ml. of ethanol for 70 min. Most of the ethanol was removed under reduced pressure and the dark brown solution was washed with ether. The aqueous layer was chilled by addition of ice and brought to pH 2 by adding *M* potassium bisulfate solution. The resulting turbid suspension was extracted with three 100-ml. portions of ethyl acetate, and the extracts were washed with brine, dried over sodium sulfate, and concentrated to a small volume, whereupon 6.15 g. of almost colorless crystals, m.p. 254–265°, precipitated. This material was dissolved in 4% aqueous sodium hydroxide, reprecipitated with *M* potassium acid sulfate, leached with 200 ml. of boiling water, and finally recrystallized from water to give the 2:1 adduct dibasic acid VIa, m.p. 270–271°. Besinet, *et al.*,⁴ report m.p. 264–265° for a 2:1 dibasic acid.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.29; H, 6.22.

The dimethyl ester VIc was prepared by treatment of VIa with a large excess of ethereal diazomethane in the presence of methanol. The mixture was filtered through Celite diatomaceous earth to remove a little insoluble material, the ether was evaporated, and the residue was recrystallized from hexane and from carbon tetrachloride to give VIc, m.p. 101–102°.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 63.86; H, 7.19.

The distilled ethyl ester fraction from the original addition (fraction A above) was saponified by heating at reflux with 300 ml. of 10% aqueous sodium hydroxide and 150 ml. of ethanol. After 1 hr., most of the ethanol was removed under reduced pressure and the aqueous residue was washed with ether, cooled well with ice, and acidified to pH 2 with *M* potassium bisulfate. The colorless precipitate of the *exo*-acid Va was allowed to coagulate, filtered, triturated with water, and dried to give 11.5 g. of material, m.p. 83–85°. Recrystallization from hexane gave 9.55 g. of material, m.p. 85–86°, reported⁵ m.p. 82.5°. Further crops taken from the mother liquor had lower melting points. The aqueous filtrate was extracted with ethyl acetate, the organic layer was washed with brine, dried over sodium sulfate, and concentrated to dryness. The residue was leached with hexane and the insoluble material, 0.51 g. of fumaric acid (identified by the infrared spectrum), was filtered off. Evaporation of the filtrate left a viscous residue, fraction B (6.2 g.); a small portion was converted to the methyl esters with ethereal diazomethane and the product analyzed by v.p.c. The major peaks corresponded in retention time to those of IVc and Vc. Small peaks corresponding to dimethyl maleate and dimethyl fumarate also were present. Among the peaks for trace components were two corresponding in retention times to those of the 2-norbornene-7-carboxylic esters VIIc and VIIIc.

The main portion of fraction B was treated with sufficient 10% aqueous sodium carbonate to dissolve it, and an equal volume of saturated aqueous sodium bicarbonate was added. A solution of iodine (0.7 *M*) in aqueous potassium iodide (2.4 *M*) was added until the yellow color disappeared only slowly. The resulting colorless precipitate of iodolactone was filtered and washed with water. Crops from several batches of fraction B had melting points varying from 129–131° dec. to 134–136° dec., reported⁴ m.p. 129–131°. They had a strong infrared absorption at 5.68 and a shoulder at 5.82 μ . Some of the crops turned yellow on standing overnight.

The aqueous filtrate from the iodolactonization was washed with chloroform, cooled with ice, and acidified with 10% sulfuric acid, whereupon a precipitate of crude *exo*-acid Va was formed. This was filtered, washed with water, dried, and recrystallized from hexane to give material, m.p. 85–86°, infrared spectrum identical with that of the sample of Va described above. From samples of fraction B totaling 18.7 g. there were obtained 7.2 g. of iodolactone and 5.5 g. of pure *exo*-acid Va.

The *endo*-acid IVa was regenerated when a solution of 5.5 g. of iodolactone in 150 ml. of acetic acid was stirred for 10 min. with 4.5 g. of zinc dust. The mixture was filtered, the filter cake was rinsed with acetone, and the combined filtrate and washings concentrated *in vacuo*. Ethyl acetate was added to the residue and the solution concentrated again. The residue was thoroughly shaken with cold 5% aqueous sodium carbonate and methylene chloride. The insoluble material was removed by filtration, and the aqueous layer separated, acidified with 10% sulfuric acid, and

extracted thrice with ether. The ether layer was washed with brine, dried over sodium sulfate and evaporated, and the residue, a colorless solid, was recrystallized from pentane to give 1.5 g. of material, m.p. 83–84°. Two further crystallizations afforded a sample of pure IVa, m.p. 83.5–84.5°. Admixture with the *exo* isomer Va caused a depression to m.p. 45–65°.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.61; H, 7.31.

The *endo*-methyl ester IVc was prepared from IVa with ethereal diazomethane. After having been washed with 10% sodium carbonate and then with water and dried over sodium sulfate, the ether solution was evaporated and the liquid residue distilled bulb-to-bulb (bath at 85–95°, 25 mm.). The infrared spectrum showed a strong band at 5.76 and a weak one at 6.07 μ .

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.71; H, 8.00.

The *exo*-methyl ester Vc was prepared from Va in the same manner. Although the esterification deliberately avoided the use of excess diazomethane for fear of attack on the double bond, 85–96% yields of Vc were achieved by recycling the unreacted acid. The ester Vc was distilled to give a colorless liquid, b.p. 108–111° (25 mm.), vapor chromatographically homogeneous. The substance showed infrared absorption at 5.78 (strong) and 6.08 μ (weak); it became yellow and viscous after storage for several weeks at room temperature and was no longer totally soluble in ether. The pyrolysis experiments were all carried out on freshly distilled material.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.84; H, 8.00.

Hydrogenation of *endo*- Δ^2 -norcarene-7-carboxylic acid (IVa) to *endo*-norcarene-7-carboxylic acid (IXa) was achieved by stirring an ethyl acetate solution of 120 mg. of pure IVa in a hydrogen atmosphere in the presence of Adams catalyst (platinum oxide) for 10 min., whereupon hydrogen absorption ceased. The catalyst was filtered off and rinsed with ethyl acetate, and the combined filtrate and washings concentrated to dryness *in vacuo*. The solid residue was recrystallized from pentane to give 75 mg. of material, m.p. 79–80°, reported¹¹ m.p. 77–78°. The mother liquors contained more IXa as well as about 10% of cyclohexylacetic acid as was shown by v.p.c. (on TCEP) of the methyl esters prepared by diazomethane treatment of the solid residue obtained after evaporation. Analogous hydrogenolyses of cyclopropanes are not uncommon, having been observed recently by Meinwald, *et al.*⁴⁸ We found that hydrogenolysis also occurred with the methyl esters IVc and Vc with 10% palladium-on-charcoal in ethanol, but not with platinum in ethyl acetate.

Hydrogenation of *exo*- Δ^2 -norcarene-7-carboxylic acid (Va) to *exo*-norcarene-7-carboxylic acid (Xa) was carried out in the same way, 85 mg. of recrystallized Xa, m.p. 95–96.5° (from pentane), reported^{11,12} m.p. 95–96°, being obtained from 150 mg. of Va. The mother liquors contained (v.p.c. on TCEP of the methyl esters) Xa (ca. 90%), cyclohexylacetic acid (ca. 10%), and a minor impurity (trace).

Epimerization of *endo*- to *exo*-7-Carbomethoxy- Δ^2 -norcarene. A. Base Catalyzed.—A solution of sodium methoxide (from 150 mg. of sodium) in 25 ml. of methanol was treated with 200 mg. of the *endo*-ester IVc and heated on the steam bath for 19 hr. An aliquot of 5 ml. was removed, evaporated to a small volume, treated with ice, and brought to pH 5 with 10% sulfuric acid. Extraction with ether, drying over sodium sulfate, and evaporation gave a liquid residue which v.p.c. analysis showed to contain 95% IVc and 5% Vc. The bulk of the solution was heated further (an additional 4 days). During this period all of the solvent inadvertently was lost by evaporation because of a drop in water pressure which caused the condenser cooling water to stop flowing. The residue was mainly hydrolyzed material since ether failed to extract any appreciable quantity until after acidification. The sticky solid acid so obtained was re-esterified with diazomethane. Analysis by v.p.c. (TCEP) showed that it consisted of a mixture of about one part IVc (*endo*) and two parts Vc (*exo*) methyl esters. No other substances were detected.

B. Thermal.—A 10- μ l. sample of the *endo*-ester IVc was sealed *in vacuo* in a Pyrex capillary, which was then immersed in a preheated bath held at 310°. After 2.5 min. the capillary was removed and the contents examined by v.p.c. The pyrolysate consisted of 85% Vc (*exo*), 5% IVc (*endo*), and 10% of material distributed among several minor components. After 10 min.

(48) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

of pyrolysis, only 2% of IVc remained, and the infrared spectrum of the pyrolysate was virtually identical with that of the *exo*-ester Vc. Exposure of *exo*-ester Vc to the same pyrolytic procedure for 15 min. at 310° gave a mixture containing 92% of Vc, 1% of IVc, and 7% of other pyrolysis products. At 355° or at longer reaction times, the capillaries exploded because of the accumulation of gaseous products, probably largely ethylene (see below).

Reaction of 1,4-Cyclohexadiene with Ethyl Diazoacetate.—A mixture of 15 g. of 1,4-cyclohexadiene (Aldrich), 0.35 g. of copper powder, and 2 ml. of ethyl diazoacetate in a three-necked, 250-ml. flask equipped with a dropping funnel and a Dry Ice-acetone condenser was heated to boiling (bath at 85°). Foaming began, and the bath was kept at 85–90° while more ethyl diazoacetate (to a total of 24 g.) was added dropwise during 25 min. After an additional 5 min., gas evolution ceased, whereupon the mixture was cooled, filtered through glass wool, and distilled, first at atmospheric pressure to remove a little unreacted cyclohexadiene, and then at aspirator pressure. The major fraction, 9.7 g., b.p. 118–120° (25 min.), was a clear, colorless liquid which consisted of *endo*-(XIb) and *exo*-(XIIf)-7-carboethoxy- Δ^3 -norcarene (in the ratio of about 1:7), diethyl maleate, and diethyl fumarate. The nonvolatile residue was not further investigated.

A mixture of 9.5 g. of distillate, 50 ml. of 10% aqueous sodium hydroxide, and 50 ml. of ethanol was heated on the steam bath. Almost at once, a colorless precipitate appeared. Heating was continued for 45 min. Most of the ethanol was removed under reduced pressure, and the residue was treated with ice. As 10% aqueous sulfuric acid was added, the precipitate dissolved; at about pH 6, the mixture set to a thick gel, but continued addition of acid to pH 2 gave a granular precipitate which was filtered off and dissolved in ether. After having been washed with brine, dried over sodium sulfate, and evaporated, the ether solution left 6.2 g. of a colorless solid, m.p. 70–85° (with softening at 60°). The *exo*-acid XIIa could be isolated from this material by direct crystallization from 50% aqueous methanol. However, a more efficient separation of the acids was achieved by the iodolactone method, essentially according to the procedure already described in the Δ^2 -series.

Treatment of a sodium carbonate solution of the mixed acids with iodine-potassium iodide solution produced a colorless precipitate (0.72 g.) of the iodolactone, m.p. 133–134° (shrinks at 130°). This substance had infrared bands at 5.82 (strong) and 5.95 μ (shoulder). It was not characterized further, but was reduced directly by stirring its solution in 10 ml. of acetic acid with 1.0 g. of zinc dust for 10 min. The solid was filtered off and rinsed with acetone. The combined filtrate and washings were concentrated *in vacuo*, ice water was added to the residue, and the precipitate was filtered and washed with water. The crude acid (0.32 g.) had m.p. 128–132°. It was dissolved in aqueous sodium bicarbonate, reprecipitated with acid, and recrystallized from aqueous methanol to give *endo*-acid XIa, m.p. 130–131.5°. The substance sublimed at 80° (1 mm.).

Anal. Calcd. for C₈H₁₀O₂: C, 69.54; H, 7.30. Found: C, 69.40; H, 7.07.

The *endo*-methyl ester XIc, a colorless liquid, was prepared from pure XIa by treatment with ethereal diazomethane and purified by bulb-to-bulb distillation. The analytical sample was recovered from a carbon tetrachloride solution used for n.m.r. and gave a low value for carbon.

Anal. Calcd. for C₉H₁₂O₂: C, 71.03; H, 7.95. Found: C, 70.31; H, 7.72.

The *exo*-acid XIIa was obtained when the basic aqueous layer from the iodolactone preparation was washed with methylene chloride and acidified with 10% sulfuric acid. The crude acid, 4.05 g., had m.p. 90–92°. It was twice sublimed at 70–85° (1 mm.) to give material, m.p. 91.5–92.5°.

Anal. Calcd. for C₈H₁₀O₂: C, 69.54; H, 7.30. Found: C, 69.69; H, 7.19.

Hofmann and co-workers⁴⁹ reported that the reaction of 1,4-cyclohexadiene with ethyl diazoacetate in the presence of copper in dibutyl ether solution followed by saponification gave an acid, C₈H₁₀O₂, m.p. 91.5–93°. These authors reduced their acid in ethanol solution over palladium-charcoal to cyclohexylacetic acid (2 moles consumed) and concluded that their 93° acid was therefore a cyclohexadieneacetic acid. Since their hydrogenation conditions might very well have been such as to hydrogenolyze a cyclopropane ring, it is not excluded that their 93° acid is

(49) K. Hofmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, *J. Am. Chem. Soc.*, **81**, 992 (1959).

the same as our *exo*- Δ^3 -norcarene-7-carboxylic acid (XIIa), m.p. 91.5–92.5°

The *exo*-methyl ester XIIc, prepared from pure XIIa with ethereal diazomethane, was a colorless liquid. It was purified by bulb-to-bulb distillation.

Anal. Calcd. for C₉H₁₂O₂: C, 71.03; H, 7.95. Found: C, 71.09; H, 7.74.

Hydrogenation of the *endo*-acid XIa in ethyl acetate over Adams catalyst gave *endo*-7-norcaranecarboxylic acid (IXa), m.p. 74–78°, infrared spectrum identical with that of a sample prepared from IVa. Hydrogenation of the *exo*-acid XIIa in the same manner gave *exo*-7-norcaranecarboxylic acid (Xa), m.p. 95.5–97° (from pentane), infrared spectrum identical with that of a sample prepared from Va.

Pyrolysis of *exo*-7-Carbomethoxy- Δ^2 -norcarene (Vc).—The reaction chamber consisted of a 0.5-in. diameter Pyrex tube mounted vertically and partially filled with glass beads to a height of 14 in. The tube was heated with resistance wire wrapped around an asbestos sheathing and connected to a rheostat. The internal temperature was measured with a thermocouple. The apparatus was flushed with nitrogen and brought to a steady temperature of 420–425° by supplying current to the heating coil. Then 15 g. of the ester Vc was dripped slowly through the reaction chamber during 30 min. The effluent pyrolysate was collected in three consecutive traps cooled at 0° (ice-water), –80° (Dry Ice-acetone), and –127° (*n*-propyl alcohol slush). The last trap was filled with stainless steel saddles. The material in the 0° trap was recycled ten times more in the same way, after which treatment the vapor chromatogram showed that most of the starting material had reacted.

Pyrolysis Products Trapped at 0°.—A small portion of the pyrolysate from the 0° trap was immediately hydrogenated in ethyl acetate solution with Adams catalyst. The hydrogenation was allowed to proceed 17 hr., whereupon the catalyst was filtered off and the filtrate evaporated. The resulting clear colorless liquid was analyzed by v.p.c. with the results shown in Table II. High accuracy is not claimed for these data, since although the v.p.c. analysis is accurate, the concentration step may have caused some fractionation by evaporation of the more volatile components.

When the mixture was hydrogenated an additional 19 hr., the portion of the product referred to in Table II as "others," *i.e.*, unidentified components, decreased. The hydrogenated material still reacted with permanganate. None of the v.p.c. peaks of the hydrogenation product corresponded in retention time to those of authentic methyl *m*-toluate, methyl β -cyclopentylpropionate, or methyl caprylate. One of the minor peaks, which constituted less than 0.05% of the total, had the same retention time as methyl 2-ethylhexanoate (3-carbomethoxyheptane).

The pyrolysis column was washed with ether and the resulting solution evaporated to dryness and combined with the contents of the 0° trap to give 12.2 g. of material. This was separated by distillation into two fractions: (a) 8.8 g. of a clear, pale yellow liquid, b.p. 75–88° (6–5 mm.); (b) 2.15 g. of a thick yellow oil, b.p. up to 110° (1 mm.).

Fraction b deposited 1.45 g. of a solid, m.p. 56–68°, when taken up in pentane and seeded with the dimer XIV of methyl cyclopentadienecarboxylate. The crude solid material was chromatographed on alumina (Merck). Benzene, 2% ether in benzene, and 5% ether in benzene eluted oily fractions, but 20% ether in benzene eluted a solid which after two recrystallizations from hexane afforded 0.42 g. of XIV, m.p. 82–82.5°; when mixed with an authentic sample of m.p. 81–83°, reported^{16b} m.p. 85°, the melting point was 81–83°. The infrared spectrum was identical with that of authentic XIV.

The pentane mother liquors from the crystallization of crude XIV were evaporated to give 0.7 g. of residue, which was chromatographed as above to give more XIV and 50 mg. of the isomeric dimer XV, m.p. 104–105.5° (soft at 102°) after three recrystallizations from hexane, reported^{16b} m.p. 103–104°. The ultraviolet spectrum showed λ_{\max} 228 m μ , in agreement with that reported.^{16b}

Fraction a of the pyrolysate from the 0° trap showed peaks in the v.p.c. corresponding to toluene, methyl *o*-toluate, methyl *p*-toluate, methyl phenylacetate, and a large number of others. The material (7.3 g.) was divided into eleven fractions by preparative v.p.c. with the PDEAS column, which was kept at 150° and purged with 200 ml./min. of helium. The traps were kept at –80°, and the total recovery was 63%. Identification of the known components of each fraction was made by comparisons of

infrared spectra and v.p.c. retention times (on the capillary column) with those of authentic samples in all cases. Where appropriate, ultraviolet and n.m.r. spectra were also examined, as indicated below. Some of the fractions gradually changed in composition after standing for 2 weeks.

Fraction 1, ca. 20 mg., was not investigated.

Fraction 2, ca. 20 mg., had the same retention time as *anti*-7-carbomethoxy-2-norbornene (VIIIc), but its infrared spectrum was different, lacking absorption in regions where VIIIc absorbed strongly. The substance seemed to be unstable under the pyrolysis conditions, since its v.p.c. peak did not increase in intensity after the first pass of Vc through the pyrolysis chamber. It had λ_{\max} 224 m μ .

Fraction 3, ca. 50 mg., consisted mainly of methyl cyclopentadienecarboxylate (XIII). After standing for 2 days, the material had the same infrared spectrum as that of the major dimer XIV. The dimer XIV decomposed at high injection port temperatures in attempted v.p.c. The monomer was readily detectable in fresh pyrolysate, but the v.p.c. peak grew weaker as the pyrolysate was allowed to stand.

Fraction 4, 0.17 g., and **fraction 5**, 0.26 g., contained several components, some of which were unstable, since the v.p.c. patterns changed after several days of storage. These materials were not further investigated.

Fraction 6, 0.30 g., consisted mainly of two substances. Upon hydrogenation it gave a material whose v.p.c. showed two main peaks (in the ratio of about 3:2) corresponding to methyl 2-methylcyclohexanecarboxylate and methyl cyclohexylacetate.

Fraction 7, 0.95 g., contained two major components and a number of minor ones. It had λ_{\max} 270 m μ in the ultraviolet spectrum. Hydrogenation of a small portion gave material whose v.p.c. showed peaks corresponding to methyl cyclohexylacetate (XVII) (34%), methyl 2-methylcyclohexanecarboxylate (20%), some of the corresponding aromatics, an unidentified component (22%), and several minor components. A sample of 0.250 g. of fraction 7 was taken up in a few ml. of ether and treated with a solution of about 0.2 g. of tetracyanoethylene in ether. The solution became red, and the ether was displaced by adding benzene and distilling. The resulting deep yellow solution was heated at reflux for 30 min. and then allowed to stand overnight, after which time the color had faded to pale yellow. The material obtained after evaporation of the solvent was chromatographed on alumina (Merck). A fraction eluted by 5% ether in benzene gave a solid, m.p. 113–145°. Later fractions eluted with more ether-rich solvents gave only oils. The crystalline material was rinsed with a little ether-pentane and recrystallized four times from benzene-hexane to give the tetracyanoethylene-cyclohexadienylacetic ester adduct XX, m.p. 163–165° (soft at 150°). The substance had no maximum above 210 m μ in the ultraviolet. The n.m.r. spectrum showed two vinyl hydrogens (at 6.7 p.p.m.), three methyl ester hydrogens (singlet at 3.78 p.p.m.); one bridgehead hydrogen (multiplet centered at about 3.56 p.p.m.); two nonequivalent methylene hydrogens α to carboxylic ester (an AB pattern⁵⁰ with J_{AB} 15 c./sec., $\Delta\nu$ = 19 c./sec., centered at 3.06 p.p.m.); and four other protons (complex multiplet between 2.5 and 1.3 p.p.m.).

Anal. Calcd. for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 64.16; H, 4.41; N, 20.03.

Another sample of fraction 7 (150 mg.) was treated with tetracyanoethylene as above and the crystalline product thrice recrystallized from benzene-hexane to give material, m.p. 147–150°. This was a mixture of compound XX and another substance. The n.m.r. spectrum showed all of the absorptions due to XX and additional bands assigned as follows: one vinyl proton (doublet centered at 7.48 p.p.m.), three methyl ester protons (singlet at 3.87 p.p.m.), three C-methyl protons (singlet at 1.92 p.p.m.), 5 other protons. The ultraviolet spectrum showed no maximum above 210 m μ .

The hydrogenation data described above show that two of the major components of the diene mixture in fraction 7 have the 2-methylcyclohexanecarboxylic and cyclohexylacetic skeletons. Since the above second tetracyanoethylene adduct contains a C-methyl group, it probably is derived from the former skeleton. If this is assumed, the absence of spin-spin splitting of the n.m.r. C-methyl signal limits the possible structures of the adduct to those derived from XXVIII, XXIX, 2-methyl-3-carbo-

methoxycyclohexadiene-1,3, and 5-methyl-6-carbomethoxy-cyclohexadiene-1,3. The latter two are, however, eliminated because they would not give an adduct with one vinyl proton. It might be expected that XXVIII, having an extended conjugated system, would show an ultraviolet absorption maximum in the 290–300 m μ region.⁵¹ The absence of ultraviolet maxima beyond 270 m μ in fraction 7 suggests that XXVIII is not a major component. This would seem to leave structure XXIX as the sole survivor; the tetracyanoethylene adduct would then be XXVII. At first glance, structure XXVII does not appear to be in complete accord with the facts, since the α,β -unsaturated ester function might be expected to produce an ultraviolet maximum above 210 m μ (compare compound XIV,^{16b} λ_{\max} 216 m μ). However, it is conceivable that steric hindrance between the CO_2CH_3 and CH_3 groups could produce enough deviation from coplanarity of the chromophore to cause a hypsochromic shift. Further support for XXVII is provided by the n.m.r. chemical shift difference between the vinyl proton absorption and that of the companion adduct XX, which has no β -carbomethoxy group. The vinyl absorption of the former adduct occurs at about 0.8 p.p.m. lower field than that of XX. The same kind of deshielding by a CO_2CH_3 substituent is observed in the two carbomethoxycyclopentadiene dimers XIV and XV, the norbornene vinyl absorption of the latter occurring at about 0.9 p.p.m. higher field. Further similar examples are available.⁵²

Fraction 8, 0.18 g., was a mixture of fractions 7 and 9.

Fraction 9, 0.91 g., showed two major v.p.c. peaks with retention times corresponding to those of starting material Vc and methyl *o*-toluate. It had no high intensity absorption above 250 m μ . Hydrogenation of 150 mg. of fraction 9 gave a mixture whose v.p.c. showed three main components corresponding in retention times to dihydro-Vc (40%) (*i.e.*, methyl *exo*-7-norcaranecarboxylate, Xc), methyl cyclohexylacetate (XVIII) (35%), and methyl *o*-toluate (25%). The n.m.r. spectrum of this mixture showed the absorptions expected for methyl *o*-toluate, in particular, the complex and characteristic splitting pattern in the aromatic region.

A 50-mg. sample of fraction 9 was heated at reflux for 1 hr. with dilute methanolic sodium methoxide, cooled in ice, neutralized, concentrated *in vacuo*, and the residue extracted with ether. After having been dried over sodium sulfate, the ether solution was evaporated to give an oily residue, λ_{\max} 264 m μ . This material showed v.p.c. peaks with the same retention times as fraction 9 but these had different intensities.

A mixture of 200 mg. of fraction 9 and 80 mg. of tetracyanoethylene was allowed to react in the manner described above for the preparation of tetracyanoethylene adducts. The resulting reddish oil was chromatographed on alumina. Benzene eluted 150 mg. of a colorless liquid which had a v.p.c. corresponding to that of the starting fraction 9. Hydrogenation gave material whose v.p.c. corresponded to that of hydrogenated fraction 9 (see above).

The remainder of fraction 9 was chromatographed on alumina; 50% benzene-pentane eluted 30 mg. of pure methyl *o*-toluate (identified by infrared, v.p.c., and n.m.r.), followed by a mixture which had λ_{\max} 264 m μ . The methyl *o*-toluate was saponified with hot aqueous methanolic sodium hydroxide for 45 min., the methanol was evaporated, the residual solution was filtered and acidified to give a solid, m.p. 103–103.5°, alone or mixed with authentic *o*-toluic acid (Aldrich).

Fraction 10, 1.47 g., showed one major v.p.c. peak (65%) and three minor ones. Two of the minor peaks corresponded in retention time to methyl *p*-toluate (9%) and methyl phenylacetate (14%). The fraction had high intensity absorption at 305 m μ . Hydrogenation gave a mixture whose v.p.c. showed peaks corresponding in retention time to methyl 4-methylcyclohexanecarboxylate (45%, two peaks in the ratio 2:1), methyl cyclohexylacetate (26%), methyl *p*-toluate and methyl phenylacetate (13%), and an unidentified substance (6%).

A 150-mg. sample of fraction 10 was heated at reflux with 100 mg. of tetracyanoethylene in a few ml. of ether for 20 min. and left overnight. Most of the solvent was evaporated and crystallization was induced by scratching, whereupon 160 mg. of material of m.p. 195–198° dec. was obtained. Recrystallization

(51) Compare *inter alia* 2,6,6-trimethyl-1,3-cyclohexadiene-1-carboxylic acid, λ_{\max} 291 m μ (alcohol) (G. Wendt, *Ber.*, **74**, 1242 (1941)), and 1-carbomethoxy-1,3-cyclohexadiene, λ_{\max} 288 m μ (isooctane).²⁷

(52) N. S. Bhacca, L. F. Johnston, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

(50) The pattern fell between spectra 1–6 and 1–7 given by K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

from ethyl acetate gave sturdy kernels of XXXIII, the tetra-cyanoethylene adduct of methyl 4-methyl-1,3-cyclohexadiene-1-carboxylate. The substance had m.p. 203–203.5° dec. and showed no absorption maximum above 210 m μ .

Anal. Calcd. for C₁₅H₁₂N₄O₂: C, 64.28; H, 4.32; N, 19.99. Found: C, 64.18; H, 4.39; N, 19.93.

After 2 weeks of storage, fraction 10 no longer showed the v.p.c. peak of the original major component. Its ultraviolet spectrum showed λ_{\max} 234 m μ .

Fraction 11, 0.35 g., consisted of a mixture of methyl *p*-toluate (75%) and methyl phenylacetate (25%) based on v.p.c., n.m.r., and infrared analyses. It was heated on the steam bath for 15 min. in a solution of 0.2 g. of sodium hydroxide in 4 ml. of 50% aqueous methanol. Most of the methanol was distilled off, ice and 10% sulfuric acid were added, and the resulting tan precipitate (240 mg., m.p. 165–178°) was filtered off and dried. This material was sublimed at about 120° at 25 mm. and then recrystallized from water to give pure *p*-toluic acid (120 mg.), m.p. 177–178° alone or mixed with an authentic sample. Its infrared spectrum was superimposable on that of authentic *p*-toluic acid.

Pyrolysis Products Trapped at –80°.—The contents of this trap were allowed to warm to room temperature while the expanding gases were passed through ether. No significant amount of material dissolved in the ether as was shown by v.p.c. The residue in the trap showed a broad ultraviolet absorption maximum in the region 220–230 m μ , similar to that reported for the dimer (XIV) of methyl cyclopentadienecarboxylate, as well as a series of sharp peaks characteristic of benzene. The v.p.c. on both Carbowax and TCEP columns showed peaks with the retention times of benzene and cyclohexene as well as other materials.

Pyrolysis Products Trapped at –127°.—The –127° trap was allowed to warm to room temperature while the expanding gases were bubbled through a 10% solution of bromine in methylene chloride. Concentration on the steam bath gave a liquid residue which was distilled bulb-to-bulb and then had a v.p.c. retention time the same as that of authentic ethylene bromide. The infrared spectrum, except for a very weak extra absorption at 5.7 μ , was superimposable on that of ethylene bromide.

Preparation of Authentic Samples.—Methyl cyclopentadienecarboxylate (XIII) was prepared by heating the dimer XIV¹⁶ with a free flame and condensing the distillate in cold benzene. The solution was immediately subjected to v.p.c. analysis and showed, besides the solvent peak, a single peak with the same retention time as that peak in the pyrolysate from Vc which disappears after standing for a few hours.

In another cracking experiment, the distillate was collected in cold ethyl acetate and the solution was immediately hydrogenated over Adams catalyst. The resulting methyl cyclopentanecarboxylate⁵³ was a colorless liquid which was homogeneous by v.p.c.

Methyl cyclohexylacetate⁵⁴ was obtained by esterification (methanol-sulfuric acid) of the product from hydrogenation⁵⁵ of phenylacetic acid at room temperature in solvent acetic acid over

(53) K. W. F. Kohlraush and R. Skrabal, *Monatsh.*, **70**, 44 (1937).

(54) P. Sabatier and M. Murat, *Compt. rend.*, **156**, 424 (1913).

platinum. The ester was separated from the methyl phenylacetate that accompanied it by preparative v.p.c.

Similarly, the methyl 4-methylcyclohexanecarboxylates were prepared from *p*-toluic acid. The product was a mixture of methyl *p*-toluate and the two saturated substances, the latter in the ratio of 2:1.⁵⁶

Methyl 2-methylcyclohexanecarboxylate was prepared similarly from *o*-toluic acid. Its v.p.c. showed only one peak besides the small one due to methyl *o*-toluate.

Methyl 3-methylcyclohexanecarboxylate was prepared by hydrogenation of methyl *m*-toluate (from *m*-toluic acid supplied by Aldrich Chemical Co.) in acetic acid solvent over Adams catalyst. After 30 hr., the catalyst was filtered off and the solution was diluted with ice water and extracted with ether. After having been washed successively with dilute aqueous sodium hydroxide, water, and brine, the ether solution was dried over sodium sulfate and evaporated to give a liquid. This was distilled bulb-to-bulb to give material which showed three v.p.c. peaks, one of which corresponded to methyl *m*-toluate. The two peaks corresponding to the methyl 3-methylcyclohexanecarboxylates were in the intensity ratio 1:5 and had retention times the same as those of the two peaks of methyl 4-methylcyclohexanecarboxylate.

Methyl cycloheptanecarboxylate (XXXVI)⁵⁷ was obtained from cycloheptanecarboxylic acid, which in turn was prepared by carbonation of the Grignard reagent from cycloheptyl bromide (Chemicals Procurement Laboratories). The acid was converted *via* the acid chloride to the amide, m.p. 192–193°, reported⁵⁸ m.p. 192–193°.

Methyl β -cyclopentylpropionate, prepared from the acid (Fluka), showed a single v.p.c. peak which did not correspond to any of the peaks shown by the hydrogenated pyrolysate from Vc.

Methyl 3-heptanecarboxylate (methyl 2-ethylhexanoate) was obtained from the acid, which was prepared by carbonation of the Grignard reagent from 3-bromoheptane (K and K Laboratories). The major product of this process had a v.p.c. retention time the same as one of the very small peaks in the hydrogenated pyrolysate.

Controls.—Methyl *m*-toluate was passed through the pyrolysis chamber under the same conditions used for the pyrolysis of Vc. After twelve passes, it had acquired a faint yellow tinge, but its infrared spectrum was identical with that of the starting methyl *m*-toluate and the v.p.c. showed only one peak.

By the same criteria, methyl *o*-toluate was also stable under the pyrolysis conditions.

(55) R. Adams and J. R. Marshall, *J. Am. Chem. Soc.*, **50**, 1970 (1928).

(56) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1245 (1939), report the formation of predominantly *cis*-4-methylcyclohexanecarboxylic acid when *p*-toluic acid is hydrogenated at 100° in acetic acid over platinum. It is not clear whether our mixture arises from lack of stereospecificity in hydrogenation or from some epimerization during esterification.

(57) L. Ruzicka, P. Barman, and V. Prelog, *Helv. Chim. Acta*, **34**, 401 (1951).

(58) T. Steadman, *J. Am. Chem. Soc.*, **62**, 1606 (1940).

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Mechanism of Transalkylation of Ethylbenzene with Gallium Bromide-Hydrogen Bromide¹

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RECEIVED DECEMBER 16, 1963

The kinetics of transalkylation of ethylbenzene-ring-C¹⁴ in benzene at 50° as followed by loss of radioactivity is first order each in hydrocarbon, gallium bromide, and hydrogen bromide. Reproducibility was good within any one series of kinetic runs but poor from one series to the next. This behavior is consistent with the carbonium ion chain alkylation-dealkylation mechanism for transalkylation that results from the identity of the rates of racemization and of loss of radioactivity with optically active ethylbenzene- α -*d*-ring-C¹⁴ and the somewhat slower scrambling of deuterium yielding ethylbenzene and ethylbenzene- α -*d*₂.

Many alkyl-aromatic compounds are known to disproportionate under acidic conditions; the alkyl group

transfers from one aromatic ring to another. For secondary alkyl compounds, the transfer seems clearly to involve the essentially free alkyl cation (σ -complex).²

(1) This work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. This paper is Part XIII of the series "Stereochemistry of the Primary Carbon."

(2) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).