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Ultraviolet and Nuclear Magnetic Resonance Spectra of 3-Phenylbornadiene-2-carboxylic Acids and 3-Phenylbornene-2-carboxylic Acids

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A series of *ortho*- and *para*-substituted 3-phenylbornadiene-2-carboxylic acids and 3-phenylbornene-2-carboxylic acids were synthesized and their ultraviolet and n.m.r. spectral properties investigated. From the ultraviolet and n.m.r. spectral data it is concluded that the two substituents possess a greater degree of coplanarity with the double bond in the norbornene series. The ultraviolet spectral characteristics of this more extensive investigation reinforce the suggestion of previous workers that there is π -bond interaction in the excited state of the norbornadienes.

Introduction

Anomalous ultraviolet spectral properties of a number of bridged polycyclic olefins have previously been reported. Jones, Mansfield, and Whiting² and Cristol and LaLonde³ observed that some derivatives of norbornene, norbornadiene, and bicyclo[2.2.2]octene exhibited longer wave length absorption maxima than similarly substituted cyclohexene, cyclopentene, and acyclic olefinic derivatives. One explanation given for the observations was based on a general destabilization of the ground and excited states, but a preferential stabilization of the highly polarized excited state was attributed to the geometry of the bridged bicyclic system.² Additional factors cited were non-classical π -bond interaction in excited states of the bridged polycyclic dienes² and the greater ability of the chromophoric system of the diene to assume coplanarity than was possible in the acyclic and monocyclic model compounds.³

In view of the limited number of examples studied, we wished to examine the generality of the long wave length absorption maxima and obtain further information as to its origin. To this end a series of 3-phenylbornadiene-2-carboxylic acids bearing substituents in the phenyl ring have been synthesized. Hydrogenation of the 5,6-double bond of each of these compounds has been carried out giving a series of dihydro derivatives, 3-phenylbornene-2-carboxylic acids. In addition to determining their ultraviolet spectra, n.m.r. spectra of all compounds were obtained to provide evidence as to the ground-state characteristics of the molecules.

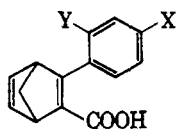
Synthesis.—Phenylpropionyl chlorides and methyl and ethyl phenylpropionates reacted with cyclopentadiene under various conditions to give Diels–Alder products which were subsequently hydrolyzed to afford the desired 3-phenylbornadiene-2-carboxylic acids (1–8). Only the preparation of 3-(*o*-nitrophenyl)-

norbornadiene-2-carboxylic acid (9) was accomplished directly by the reaction of the phenylpropionic acid and cyclopentadiene. The elemental analyses, neutralization equivalents, and infrared and n.m.r. spectra were consistent with the structures of the newly synthesized compounds. All 3-phenylbornadiene-2-carboxylic acids exhibited bands at 6.40 ± 0.05 and $14.13 \pm 0.09 \mu$ in the infrared. These bands are characteristic of an unsubstituted carbon–carbon double bond in a norbornane ring.⁴ Details of the n.m.r. spectra are given in another section of this paper.

The selective catalytic hydrogenation of the unsubstituted carbon–carbon double bond of the 3-phenylbornadiene-2-carboxylic acids gave the 3-phenylbornene-2-carboxylic acids, 1-H₂ to 9-H₂. These compounds exhibited no absorption bands in the regions of 6.4 and 14.1 μ .

The carbonyl stretching band of all the carboxylic acids in chloroform and carbon tetrachloride solutions or potassium bromide pellets was found at $5.98 \pm 0.03 \mu$ with no apparent difference in the position of the band for norbornadiene and norbornene derivatives. Interestingly, all the carbonyl bands fall at longer wave lengths than do the carbonyl bands ($5.92 \pm 0.02 \mu$) of the corresponding *ortho*- and *para*-substituted *trans*-cinnamic acids.

Ultraviolet Spectra.—As the spectral data in Table I indicate, 3-phenylbornadiene-2-carboxylic acid and all the *p*-substituted 3-phenylbornadiene-2-carboxylic acids give lower intensity absorption maxima at longer wave lengths than do the corresponding 3-phenylbornene-2-carboxylic acids. In turn, the spectra of the 3-phenylbornene-2-carboxylic acids give lower intensity absorption maxima at wave lengths longer than or equal to the corresponding *trans*-cinnamic acids. These spectral differences are exemplified in the comparison of the spectra given in Fig. 1. The spectral properties of the *trans*-cinnamic acids are considered appropriate for comparison in the sense that the skeletal chromophore in the *trans*-cinnamic acids has a greater tendency toward coplanarity than does the same chromophore in the *cis*-cinnamic acids.⁵ The *trans*-cinnamic acids serve then as the best available models of coplanar ArC=CCOOH chromophores.⁶



- 1, Y = H, X = H³
 2, Y = H, X = CH₃
 3, Y = CH₃, X = H
 4, Y = H, X = CH₃-O-
 5, Y = CH₃-O-, X = H

- 6, Y = H, X = Cl
 7, Y = Cl, X = H
 8, Y = H, X = NO₂
 9, Y = NO₂, X = H

(1) Syracuse University.

(2) E. R. H. Jones, C. H. Mansfield, and M. Whiting, *J. Chem. Soc.*, 4073 (1956).

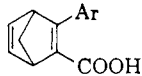
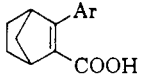
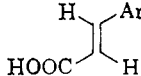
(3) S. J. Cristol and R. T. LaLonde, *J. Am. Chem. Soc.*, **81**, 5417 (1959).

(4) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(5) For original references see E. A. Braude, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **42**, 126 (1945).

(6) There is some difficulty in choosing models among known compounds for a *cis*-ArC=CCOOH chromophoric system which are devoid of steric inhibition to coplanarity. *cis*-Cinnamic acids as well as α,β -dialkylcinnamic acids of either configuration exhibit ultraviolet spectral properties which indicate a twisted chromophore. The *trans*-cinnamic acids, independent of

TABLE I
 ULTRAVIOLET SPECTRA OF ArC=CCOOR DERIVATIVES

Ar						
	λ_{\max} , m μ	$\epsilon \times 10^{-3}$	λ_{\max} , m μ	$\epsilon \times 10^{-3}$	λ_{\max} , m μ	$\epsilon \times 10^{-3}$
C ₆ H ₅ -	284	8.70	276	11.0	272	20.6
<i>p</i> -CH ₃ C ₆ H ₄ -	301	7.71	283	10.6	280	22.5
<i>o</i> -CH ₃ C ₆ H ₄ -	282	3.91	256 (sh) ^a	5.50 (sh) ^a	270	16.7
<i>p</i> -CH ₃ OC ₆ H ₄ -	317	9.65	298	10.5	298	19.8
<i>o</i> -CH ₃ OC ₆ H ₄ -	307	5.00	268	4.93	274	13.0
<i>p</i> -ClC ₆ H ₄ -	294	7.86	281	12.2	277	20.5
<i>o</i> -ClC ₆ H ₄ -	276	3.76	244 (sh)	7.55 (sh)	270	18.7
<i>p</i> -NO ₂ C ₆ H ₄ -	327	10.7	314	11.6	296	15.8
<i>o</i> -NO ₂ C ₆ H ₄ -	306 (sh)	2.96 (sh)	307 (sh)	2.80 (sh)	307 (sh)	3.15 (sh)

^a sh indicates center of shoulder.

Whereas the *ortho*-substituted 3-phenylnorbornadiene-2-carboxylic acids (except the *o*-nitro derivative) give absorption maxima, three of the four *ortho*-substituted 3-phenylnorbornene-2-carboxylic acids show only a shoulder above 220 m μ . However, the intensity of this shoulder in every case is the same as or slightly greater than the intensity of the absorption maximum of the corresponding norbornadiene. 3-(*o*-Methoxyphenyl)norbornene-2-carboxylic acid is the single *ortho*-substituted 3-phenylnorbornene-2-carboxylic acid which exhibits an absorption maximum, but the maximum is shifted to shorter wave lengths by nearly 40 m μ compared to the norbornadiene counterpart and the extinction coefficients are the same. Spectra of the *o*-tolyl compounds shown in Fig. 2 illustrate the spectral differences of one series of *ortho*-substituted compounds.

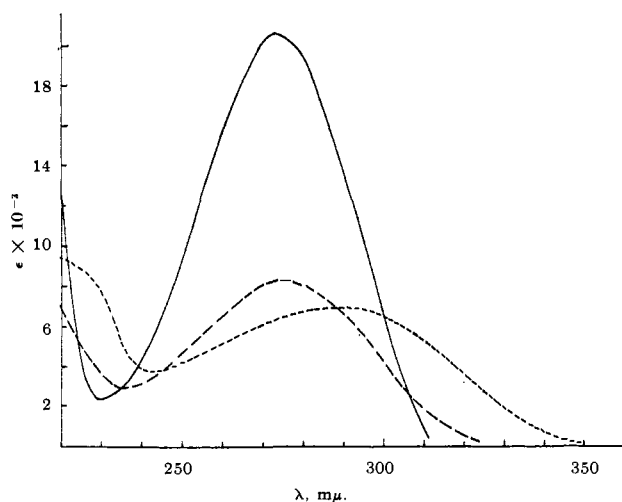


Fig. 1.—Ultraviolet spectra of: *trans*-cinnamic acid, —; 3-phenylnorbornene-2-carboxylic acid, ---; 3-phenylnorbornadiene-2-carboxylic acid, - · - ·; all compounds in 95% ethanol.

Our explanation for the above ultraviolet spectral differences of norbornadiene, norbornene, and *trans*-cinnamic acid derivatives is based on a combination of steric effects in the ground and excited states and transannular π -bond interactions in the excited state. Slight steric crowding of a chromophore generally results in a lower extinction coefficient.⁷ The decrease

steric effects, will have an extinction coefficient larger than the *cis*-acids probably as a result of an elongated chromophore. In spite of this drawback we have chosen the *trans*-acids as models because of the lack of coplanar *cis* models.

in extinction coefficients (in the order: *trans*-cinnamic acid > norbornene > norbornadiene) observed for the *p*-substituted derivatives is attributed to increasing steric interference between conjugated groups and its consequent inhibiting effect on the characteristic

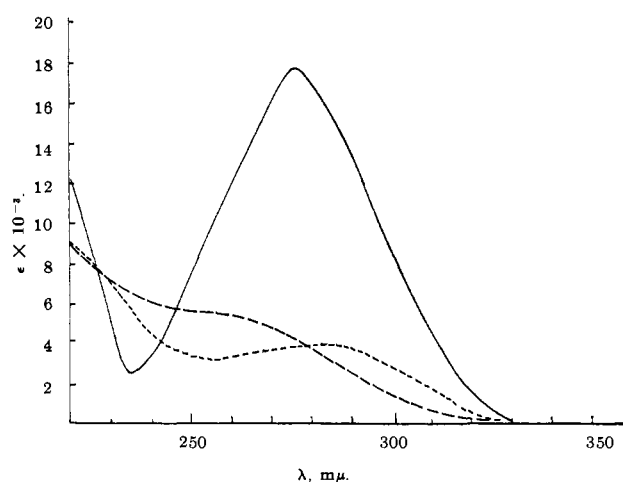


Fig. 2.—Ultraviolet spectra of: *trans*-*o*-methylcinnamic acid, —; 3-*o*-tolylnorbornene-2-carboxylic acid, ---; 3-*o*-tolylnorbornadiene-2-carboxylic acid, - · - ·; all compounds in 95% ethanol.

electronic transition. This rationale requires that there are small differences in the geometry of double bonds in norbornene and norbornadiene ring systems⁸ and is consistent with the n.m.r. results given later. The absence of absorption maxima in the spectra of some *ortho*-substituted 3-phenylnorbornene-2-carboxylic acids indicates that loss of chromophoric coplanarity is severe when groups having greater steric requirements, such as *ortho*-substituted phenyl groups, are substituted at C-3 in norbornene.

Transannular π -bond participation in the excited state has been considered in a theoretical treatment of

(7) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 15.

(8) Specifically, angle α might be smaller in norbornadiene than the



corresponding external bond angle in norbornene. On the basis of calculation and the data of Schomaker, Wilcox has proposed [*J. Am. Chem. Soc.*, **83**, 3866 (1961)] that the effect of introducing a second double bond into the norbornene ring system has very little effect on the internal bridge angles. Unfortunately, data relevant to the size of the pertinent external bridge angles do not seem to be available.

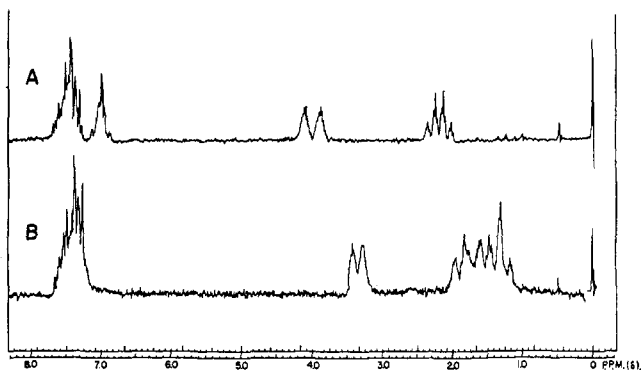


Fig. 3.—A. The n.m.r. spectra of 3-phenylnorbornadiene-2-carboxylic acid as a 10% (w./v.) solution in CDCl_3 . B. The n.m.r. spectra of 3-phenylnorbornene-2-carboxylic acid as a 10% (w./v.) solution in CDCl_3 .

the ultraviolet absorption spectrum of norbornadiene.⁹ In an extension of this work, Wilcox¹⁰ devised an interacting, nonconjugated chromophore model to explain the ultraviolet spectral differences between derivatives of 2,3-dicarboethoxynorbornadiene and 2,3-dicarboethoxy-2-norbornene. Possibly the low extinction coefficients and long wave length absorption maxima of the 3-phenylnorbornadiene-2-carboxylic acids can be explained in terms of the same model. The persistence of absorption maxima for most of the *ortho*-substituted 3-phenylnorbornadiene-2-carboxylic acids in spite of a probable greater tendency toward lack of

a coplanar $\text{Ar}-\text{C}=\text{CCOOH}$ chromophore makes transannular interaction in the excited state an essential part of this explanation regardless of the precise model for the interaction.

N.m.r. Spectra.—The spectra of **1** and **1-H₂** are shown in Fig. 3 as examples typical of all the measured spectra. Assignments of the absorption patterns to specific protons are as follows. In the spectrum of **1**, the unsymmetrical multiplet in the region of 7.3–7.8¹¹ is assigned to the protons of the phenyl group. The symmetrical peak centered at 7.0 is attributed to the two protons attached to the double bond. The bridgehead protons are responsible for the two peaks at 4.11 and 3.88, and the remaining two protons yield the AB type pattern centered at 2.17 (perturbed by the bridgehead protons which split each peak into a triplet). All features of fine structure as well as observed chemical shifts for these peaks are in accord with the previous observations on protons in bicyclic rings.^{12–14} In the spectrum of **1-H₂** only the aromatic absorption at 7.4 and the absorption multiplets at 3.42 and 3.27 attributed to the two bridgehead protons are assignable with certainty. In all likelihood the two closely spaced triplets at 1.30 and 1.16 represent the bridge proton *anti* to the double bond. The *syn* proton attached to the same carbon atom is not readily discernible due to long-range coupling with the *endo*

hydrogens on the ethylene bridge, an interaction which appears to be general.¹⁴ The phenyl-substituted derivatives **2** to **9** and their dihydro derivatives all give similar spectra.

The olefinic absorptions always appear between 7.1–6.9, and little variation in the absorption pattern of the ethylenic protons could be noted. But one striking trend is consistently observed in all the pairs of compounds. This involves the chemical shifts of the bridgehead protons which are given in Table II.

TABLE II
CHEMICAL SHIFTS OF THE BRIDGEHEAD PROTONS IN
COMPOUNDS 1–9

Compd.	Values of bridgehead protons		$\Delta\nu_a^{\text{H}_2}$	$\Delta\nu_b^{\text{H}_2}$	$\Delta\Delta\nu$
	a	b			
1	4.11	3.88	0.69	0.61	0.08
1-H₂	3.42	3.27			
2	4.09	3.87	.67	.60	.07
2-H₂	3.42	3.27			
3	4.07	3.69	.69	.61	.08
3-H₂	3.38	3.08			
4	4.10	3.89	.67	.59	.08
4-H₂	3.43	3.30			
5	4.02	3.82 ^a	.65	.60	.05
5-H₂	3.37	3.22			
6	4.10	3.84	.68	.60	.08
6-H₂	3.42	3.24			
7	4.08	3.83	.70	.61	.09
7-H₂	3.38	3.22			
8	4.18	3.93	.69	.62	.07
8-H₂	3.49	3.31			
9	4.04	3.70	.69	.62	.07
9-H₂	3.35	3.08			

^a Value is approximate since peak was partially obscured by OCH_3 absorption.

Actually a casual glance at the spectra of any pair of compounds, norbornadiene and norbornene (see Fig. 3), reveals a partial coalescence of the two bridgehead peaks in the norbornene relative to the norbornadiene. In other words, the lower field bridgehead proton a moves more to high field upon hydrogenation ($\Delta\nu_a^{\text{H}_2} = 0.69$) than does the higher field bridgehead proton b ($\Delta\nu_b^{\text{H}_2} = 0.60$). These $\Delta\nu$ values are included in Table II for each pair of compounds studied. Also the difference between their upfield shifts ($\Delta\Delta\nu = \Delta\nu_a^{\text{H}_2} - \Delta\nu_b^{\text{H}_2}$) is given. It will be noted that the two peaks consistently move closer together, $\Delta\Delta\nu = 0.07 - 0.08$ p.p.m. (The one instance where $\Delta\Delta\nu = 0.05$ for **5** is inaccurate owing to overlapping of one of the bridgehead absorption patterns by the methoxyl peak.) This consistent behavior is well outside the limits of accuracy of the measured chemical shifts, ± 0.015 , and the limits of accuracy of the $\Delta\Delta\nu$ values, ± 0.03 . Therefore the removal of the double bond has a different effect on bridgehead protons a and b. The anticipated effect of this chemical change can be estimated from the chemical shift values for norbornadiene and norbornene bridgehead protons which are 3.57 and 2.85, respectively.¹⁵ Thus they move upfield 0.72 p.p.m. upon hydrogenation, whereas the average upfield shift in our series is 0.68 for proton a and

(15) These values were obtained by actually measuring the chemical shift differences between the two bridgehead peaks; thus the errors attributed to improper adjustment of TMS and drifting are minimized.

(16) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsugi, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(9) C. F. Wilcox, Jr., S. Winstein, and N. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

(10) C. F. Wilcox and R. R. Craig, *ibid.*, **83**, 4258 (1961).

(11) All chemical shift values are reported in this paper in δ , where $\delta =$ p.p.m. from tetramethylsilane, the internal reference.

(12) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(13) H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, *J. Chem. Soc.*, 682 (1964).

(14) An article by Laszlo and Schleyer [*J. Am. Chem. Soc.*, **86**, 1171 (1964)] is recommended for a complete review of all the pertinent references to the n.m.r. spectra of bicycloheptane derivatives.

0.60 for proton b.¹⁷ Thus an upfield shift is observed in the compounds we have studied, but a secondary effect, paramagnetic in nature and of unequal intensity at the two bridgeheads, is also operative. This causes a secondary downfield shift upon the one proton of 0.04 p.p.m. and upon the other of 0.12 p.p.m. It is the origin of this secondary effect that we wish to discuss.

The anisotropy of a benzene ring has been well established.¹⁸ It causes a deshielding of protons lying in the plane of the six carbon atoms and causes shielding of those protons lying above the ring. The intensity and sign of its effect is therefore a function of the angle θ between the plane of the ring and the line joining the center of the ring with a particular proton. The observed coalescence can then be accounted for if the benzene ring becomes more planar with the double bond in the hydrogenated product than in the norbornadiene. Alternatively, increased coplanarity of the anisotropic carbonyl group with the double bond could also account for the observed effect. Since the effect of a phenyl group is stronger,¹⁸ it undoubtedly should have the major influence. In either case the observed preferential shifts upfield, smaller than expected, can be explained if the benzene ring and double bond are more coplanar in the norbornenes. Thus it is indicated that the angle α^8 is greater in the norbornenes allowing greater coplanarity of phenyl and carboxylic acid substituents.

A second possible source of the observed coalescence could be an asymmetry present in the anisotropy of the C₅-C₆ double bond so that one bridgehead proton is affected more than the other by the removal of the C₅-C₆ double bond. This would necessarily imply some transannular interaction of π -bonds in the ground state. An interaction of this type has been suggested by Tori, *et al.*,¹⁶ in order to account for the anomalous chemical shift behavior of the methylene bridge protons in the series norbornadiene, norbornene, and norbornane. The methylene bridge protons in norbornadiene appear 0.8 p.p.m. below their expected position. Actually Tori's explanation appears unsatisfactory to these authors since the bridgehead protons show no such anomaly in spite of the fact that they should be more sensitive to such a transannular effect because they are closer to it. Furthermore, the 7-hydroxynorbornadiene, norbornene pair studied by Snyder and Franzus¹⁹ appear to be normal. Finally, Turner's heat of hydrogenation data²⁰ as well as Wilcox, Winstein, and McMillan's⁹ molecular orbital calculations lead the respective authors to conclude that there is no transannular bonding interaction in the ground state of norbornadiene. For these reasons we prefer to account for the observed coalescence in terms of a twisted phenyl group.²¹

(17) The alternative possibility is that one proton moves 0.80, the other 0.46; *i.e.*, that the higher field absorption in the norbornadienes is attributed to the same proton giving the lower field absorption in the norbornene. This possibility could only be rigorously disproved by deuterium labeling experiments. However, this possibility seems extremely unlikely.

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(19) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

(20) R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(21) It has been pointed out by a referee that the ground-state magnetic properties are related to the electronic excited states according to the paramagnetic term of the Van Vleck formula [J. H. Van Vleck, "Electronic and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1962].

In summary, the ultraviolet spectral studies demonstrate that the longer wave length absorption maxima of norbornadienes is a general feature of these compounds. Furthermore, this feature is due in part to some transannular π -bond interaction in the excited state as originally suggested by Jones and later developed by Wilcox. Clearly the ultraviolet spectral properties are related also to the degree of uniplanarity of the chromophore which, according to the n.m.r. data and its interpretation, is greater in the norbornenes than in the norbornadienes. Unfortunately, the results do not provide an insight into the more subtle effects of geometry and strain on the ultraviolet spectral properties as discussed by Jones.

Experimental²²

3-Phenylnorbornene-2-carboxylic Acid.—Hydrogenation of 470 mg. of 3-phenylnorbornadiene-2-carboxylic acid⁸ (2.2 mmoles) in 30 ml. of 95% ethanol with 90 mg. of 10% palladium-on-charcoal proceeded until 1 equiv. of hydrogen had been absorbed. Recrystallization of the product from ethanol-water gave 369 mg. (72%), m.p. 113–115°. The infrared spectrum (carbon tetrachloride) showed a strong band at 6.28 μ . The characteristic norbornene absorptions⁴ at 6.39 and 14.15 μ were absent.

Anal. Calcd. for C₁₄H₁₄O₂: C, 78.48; H, 6.59; neut. equiv., 214. Found: C, 78.57; H, 6.66; neut. equiv., 215.

A solution of 861 mg. of methyl 3-phenylnorbornadiene-2-carboxylate (3.8 mmoles) in 30 ml. of 95% ethanol was hydrogenated in the presence of 60 mg. of palladized charcoal until 1 equiv. of hydrogen had been absorbed. The ethanol was removed at reduced pressure, and the residue was then distilled, b.p. 103–104° (0.17 mm.), to give 450 mg. (52%), *n*_D²⁰ 1.5725. The infrared spectrum (carbon tetrachloride) showed a strong band at 5.87 μ . Bands in the regions of 6.35 and 14.2 μ were absent.

Anal. Calcd. for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found: C, 78.92; H, 7.24.

3-*p*-Tolylnorbornadiene-2-carboxylic Acid.—Sixteen grams of *p*-tolylpropyl chloride (90 mmoles) and 7.0 g. of freshly distilled cyclopentadiene (111 mmoles) in 100 ml. of dry toluene were heated to reflux for 48 hr. When cool, the reaction mixture was stirred vigorously overnight with 5% aqueous sodium bicarbonate solution. The slightly basic aqueous layer was separated and decolorized with Norit. Subsequent acidification resulted in the precipitation of 3 g. of crude product (m.p. 127–160°) which was recrystallized four times from ethanol-water to give 1.0 g. of product, m.p. 179–181°. The infrared spectrum (carbon tetrachloride) showed bands at 5.95, 6.39, and 14.15 μ .

Anal. Calcd. for C₁₅H₁₄O₂: C, 79.62; H, 6.24; neut. equiv., 226. Found: C, 79.27; H, 6.24; neut. equiv., 226.

Quantitative hydrogenation of 3-*p*-tolylnorbornadiene-2-carboxylic acid, in the manner employed in the hydrogenation of 3-phenylnorbornadiene-2-carboxylic acid, gave 3-*p*-tolylnorbornene-2-carboxylic acid, m.p. 150–152°. The infrared spectrum (carbon tetrachloride) showed a strong band at 5.95 μ but no bands in the region 6.35 or 14.2 μ .

Anal. Calcd. for C₁₅H₁₆O₂: C, 78.92; H, 7.07; neut. equiv., 228. Found: C, 79.20; H, 7.26; neut. equiv., 215.

3-*o*-Tolylnorbornadiene-2-carboxylic Acid.—The procedure used in the preparation of the *ortho* isomer was precisely the same as that employed in the preparation of the *para* isomer. From 4.45 g. of *o*-tolylpropyl chloride and 5.0 g. of cyclopentadiene was obtained 2.0 g. of crude diene (m.p. 122–126°) which after recrystallization from ethyl acetate and acetone-water gave 1.5 g. of material, m.p. 128–129°. The infrared spectrum (carbon tetrachloride) exhibited bands at 5.98, 6.44, and 14.08 μ .

Anal. Calcd. for C₁₅H₁₄O₂: C, 79.62; H, 6.24; neut. equiv., 226. Found: C, 79.34; H, 6.01; neut. equiv., 225.

Quantitative hydrogenation of 194 mg. of the diene (0.86 mmole) in the usual manner gave 93 mg. of 3-*o*-tolylnorbornene-2-carboxylic acid, m.p. 129–131° (from water-ethanol). The infrared

Although its intrusion in the present instance cannot be rigorously disproved, the contribution of this term to the chemical shifts of protons is not normally observable.

(22) All melting points are uncorrected and were obtained in capillaries using a Mel-Temp melting point apparatus. Elemental analyses were carried out by H. Galbraith, Knoxville, Tenn.

spectrum (carbon tetrachloride) exhibited a band at 5.97 μ but no bands in the region of 6.35 or 14.2 μ .

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07; neut. equiv., 228. Found: C, 79.43; H, 6.81; neut. equiv., 229.

3-(*p*-Chlorophenyl)norbordiene-2-carboxylic Acid.—A solution of 3.1 g. of *p*-chlorophenylpropionyl chloride (15.6 mmoles) and 1.5 g. of freshly distilled cyclopentadiene in 100 ml. of dry benzene was heated to reflux for 31 hr. Work-up in the usual manner gave 2.2 g. of crude product. This material and 0.9 g. of crude product from a second reaction furnished, after chromatography on silica gel employing 50% carbon tetrachloride–chloroform as the eluting solvent, 1.4 g. of crystalline product, m.p. 110–135°. A solution of this material in acetonitrile–water gave, after prolonged standing at –5°, 1.0 g. of large transparent crystals, m.p. 140–142°. An infrared absorption spectrum (carbon tetrachloride) showed absorption bands at 5.98, 6.39, and 14.22 μ .

Anal. Calcd. for $C_{14}H_{11}ClO_2$: C, 68.15; H, 4.49; Cl, 14.37; neut. equiv., 247. Found: C, 67.96; H, 4.49; Cl, 14.17; neut. equiv., 248.

Quantitative hydrogenation of 426 mg. of 3-(*p*-chlorophenyl)norbordiene-2-carboxylic acid in the usual manner gave 3-(*p*-chlorophenyl)norbordene-2-carboxylic acid, m.p. 137–139°. Recrystallization from ethanol–water gave 250 mg. of flakes, m.p. 138–140°. The infrared spectrum (potassium bromide pellet) exhibited an absorption band at 6.00 μ but no bands in the region of 6.35 and 14.2 μ .

Anal. Calcd. for $C_{14}H_{13}ClO_2$: C, 67.60; H, 5.27; Cl, 14.26; neut. equiv., 249. Found: C, 67.29; H, 5.41; Cl, 14.10; neut. equiv., 247.

3-(*o*-Chlorophenyl)norbordiene-2-carboxylic Acid.—A solution of 5.0 g. of *o*-chlorophenylpropionic acid (25 mmoles) and 2.0 g. of freshly distilled cyclopentadiene (36 mmoles) in 120 ml. of dry benzene was heated to reflux for 41 hr. After work-up of the reaction mixture in the usual manner, 1.2 g. of diene, m.p. 125–126°, was obtained. This material when dissolved in hot naphtha solvent, treated with Norit, and cooled gave 640 mg. of diene, m.p. 125–127°. The infrared spectrum (chloroform) showed bands at 5.95, 6.39, and 14.17 μ .

Anal. Calcd. for $C_{14}H_{11}ClO_2$: C, 68.15; H, 4.49; Cl, 14.37; neut. equiv., 247. Found: C, 68.02; H, 4.46; Cl, 14.26; neut. equiv., 245.

Quantitative hydrogenation of 373 mg. of the diene gave 450 mg. of 3-(*o*-chlorophenyl)norbordene-2-carboxylic acid, m.p. 121–123° (from ethanol–water). The infrared spectrum (potassium bromide pellet) exhibited a band at 5.95 μ , but no bands in the region of 6.35 and 14.2 μ .

Anal. Calcd. for $C_{14}H_{11}ClO_2$: C, 67.60; H, 5.27; Cl, 14.26; neut. equiv., 249. Found: C, 67.85; H, 5.28; Cl, 14.02; neut. equiv., 248.

3-(*p*-Methoxyphenyl)norbordiene-2-carboxylic Acid.—Methyl *p*-methoxyphenylpropionate (4.6 g., 0.024 mole) and 2.0 g. of freshly distilled cyclopentadiene (0.03 mole) in 90 ml. of *o*-dichlorobenzene was heated in a sealed glass tube for 53 hr. at 179°. The solvent was removed at reduced pressure and the residue on distillation gave fraction 1, b.p. 75–130° (0.07 mm.), 0.29 g., and fraction 2, b.p. 130° (0.05 mm.), 5.34 g. Redistillation of fraction 2 gave two fractions. The first fraction, b.p. 124–130° (0.05 mm.), 0.722 g., contained unconverted methyl acrylate as evidenced by the band at 4.50 μ in the infrared spectrum. The second fraction, b.p. 130–138° (0.05 mm.), 3.15 g., exhibited bands at 5.85, 6.37, and 14.01 μ , but no bands in the region of 4.5 μ . A portion of the latter fraction (1.7 g., 6.6 mmoles) was added to 60 ml. of a solution of potassium hydroxide (0.02 mole) in water–methanol and the resulting solution was heated to reflux for 2 hr., cooled, diluted with 100 ml. of water, and extracted with ether to remove unconverted ester. The aqueous portion was acidified and extracted with 30-ml. portions of ether. The combined ether extracts were dried over calcium chloride. Removal of the ether at reduced pressure gave a solid residue, which by recrystallization from benzene afforded 1.2 g. of solid melting over a wide range (95–126°). This impure material was dissolved in aqueous sodium bicarbonate and the resulting solution was extracted with ether and then acidified, whereupon 400 mg. of solid, m.p. 131–134°, was obtained. Material of m.p. 136–137.5° was obtained after two subsequent recrystallizations from acetone–water. An infrared spectrum (carbon tetrachloride) showed bands at 6.00, 6.44, and 14.08 μ .

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.37; H, 5.82; neut. equiv., 242. Found: C, 74.20; H, 5.95; neut. equiv., 242.

Quantitative hydrogenation of 550 mg. of the diene in ethanol solution employing a palladium-on-charcoal catalyst gave 300 mg. of 3-(*p*-methoxyphenyl)norbordene-2-carboxylic acid, m.p. 145–146°. The infrared spectrum (carbon tetrachloride) showed a strong band at 5.99 μ but no bands in the region of 6.35 and 14.2 μ .

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.76; H, 6.60; neut. equiv., 244. Found: C, 73.36; H, 6.65; neut. equiv., 244.

3-(*o*-Methoxyphenyl)norbordiene-2-carboxylic Acid.—*o*-Methoxyphenylpropionyl chloride (4.14 g., 0.0216 mole) and 2.0 g. of freshly distilled cyclopentadiene in 120 ml. of dry benzene was heated to reflux for 41 hr. Work-up in the manner described for other syntheses involving acid chlorides gave 900 mg. of crude solid product obtained as a first crop, m.p. 126–131° (500 mg.), a second crop, m.p. 140–142° (200 mg.), and a third crop, m.p. 137–140° (200 mg.). Repeated recrystallization of the first crop from acetone–water afforded 180 mg. of material, m.p. 148–149°. The infrared spectrum (carbon tetrachloride) showed absorption bands at 5.98, 6.40, and 14.07 μ .

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.37; H, 5.82; neut. equiv., 242. Found: C, 74.14; H, 5.89; neut. equiv., 244.

The diene (336 mg.) in 25 ml. of ethanol gave after quantitative hydrogenation 200 mg., m.p. 128–130° (acetone–water), of 3-(*o*-methoxyphenyl)norbordene-2-carboxylic acid. The infrared spectrum (carbon tetrachloride) showed a strong band at 5.98 μ . No bands were observed in the 6.39 and 14.20 μ regions.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.76; H, 6.60; neut. equiv., 244. Found: C, 73.58; H, 6.46; neut. equiv., 244.

3-(*p*-Nitrophenyl)norbordiene-2-carboxylic Acid.—A solution of 2.4 g. of ethyl *p*-nitrophenylpropionate (11 mmoles) and 2.0 g. of freshly distilled cyclopentadiene (30 mmoles) in 50 ml. of dry toluene was heated to reflux for 40 hr. The residue obtained after removal of the toluene at reduced pressure was chromatographed on a column packed with 21 g. of neutral alumina. The column was eluted first with 50 ml. of hexane and then with 25% benzene–75% *n*-pentane; 2.23 g. of a yellow solid, m.p. 63–66°, was eluted. The infrared spectrum (chloroform) of this material showed bands at 6.28, 6.30, and 14.04 μ . No bands were observed in the triple bond region.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.31; N, 4.91. Found: C, 67.53; H, 5.45; N, 4.85.

Treatment of 2.23 g. of ethyl 3-(*p*-nitrophenyl)norbordiene-2-carboxylate with 75 ml. of a solution of potassium hydroxide (24 mmoles) in 90% ethanol heated to reflux for 2 hr. resulted, after work-up, in the formation of 1.48 g. of solid acid, m.p. 128–138°. Repeated recrystallization from ethyl acetate and ethyl acetate–petroleum ether gave material melting at 142–143.5°. The infrared spectrum (chloroform) of the acid showed bands at 5.98, 6.41, and 14.17 μ .

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45; neut. equiv., 257. Found: C, 65.61; H, 4.23; N, 5.22; neut. equiv., 256.

Quantitative hydrogenation of 690 mg. of ethyl 3-(*p*-nitrophenyl)norbordiene-2-carboxylate in ethyl acetate solution gave 690 mg. of a solid, m.p. 81–86°. This material was subsequently saponified by treatment with a solution of 450 mg. of potassium hydroxide in 50 ml. of 90% ethanol. 3-(*p*-nitrophenyl)norbordene-2-carboxylic acid (535 mg.) was obtained as a crystalline solid, m.p. 136–137°. The infrared spectrum (potassium bromide pellet) showed a band at 5.94 μ but no bands in the region of 6.35 and 14.2 μ .

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.40; neut. equiv., 259. Found: C, 65.02; H, 5.05; N, 5.03; neut. equiv., 261.

3-(*o*-Nitrophenyl)norbordiene-2-carboxylic Acid.—A solution of 4.0 g. of *o*-nitrophenylpropionic acid (21 mmoles) and 3.0 g. of freshly distilled cyclopentadiene (45 mmoles) in 120 ml. of dry benzene was heated to reflux for 24 hr. The residue obtained after removing the benzene at reduced pressure was dissolved in ether and the resulting solution was shaken with 5% aqueous sodium bicarbonate solution. The aqueous solution was treated with charcoal and then acidified. Obtained was 5.0 g. of a solid, m.p. 140–153°. Recrystallization of the crude diene acid from ethyl acetate gave a first crop (800 mg.), m.p. 185–187° dec., and a second crop (1.20 g.), m.p. 154–165°. Recrystallization of the first crop from ethyl acetate afforded 690 mg. of diene acid, m.p. 188–190° dec. The infrared spectrum (chloroform) showed bands at 5.98, 6.37, and 14.12 μ .

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45; neut. equiv., 257. Found: C, 65.25; H, 4.30; N, 5.27; neut. equiv., 254.

Quantitative hydrogenation of 479 mg. (18.6 mmoles) of the diene in ethyl acetate solution was carried out over palladium-on-charcoal until 1 equiv. of hydrogen had been taken up. The solvent was evaporated at reduced pressure until the volume of solution remaining was 8 ml. This solution was allowed to stand at -5° overnight. In this manner was obtained 230 mg. of straw-colored crystals, m.p. $176-178^\circ$. This material and an additional 150 mg. of material obtained as a second crop were chromatographed on a silica gel column. Elution was carried out using 80 ml. of carbon tetrachloride, 50 ml. of 25% chloroform-75% carbon tetrachloride, 50 ml. of 50% chloroform-50% carbon tetrachloride, 50 ml. of chloroform, 50 ml. of 50% ether-50% chloroform. No bands came off the column until the last solvent system was used. The material obtained, 301 mg., was recrystallized from carbon tetrachloride giving 3-(*o*-nitrophenyl)-norbornene-2-carboxylic acid, m.p. $176-177.5^\circ$. The infrared spectrum (carbon tetrachloride) showed a band at 5.96μ but no bands at 6.35 and 14.2μ .

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 64.85; H, 5.05; N, 5.40; neut. equiv., 259. Found: C, 64.95; H, 5.20; N, 5.35; neut. equiv., 258.

Spectroscopic Studies.—Ultraviolet absorption data were determined with a Cary recording spectrophotometer, Model 15, employing 95% ethanol as a solvent. The *trans*-cinnamic acids used in these studies were purchased or prepared according to well-known methods described in the literature. Infrared spectra were determined with a Baird infrared spectrophotometer using carbon tetrachloride and chloroform solutions and in some cases potassium bromide pellets. The n.m.r. spectra were obtained from a Varian Model A-60 employing deuterated chloroform as the solvent and tetramethylsilane as an internal standard. Concentrations of 10% (w./v.) were employed throughout and more dilute solution spectra (5%) were also measured in the case of **3**, **3-H₂**, **8**, and **8-H₂**. There was no observable dilution effect on the τ -values.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILLINOIS]

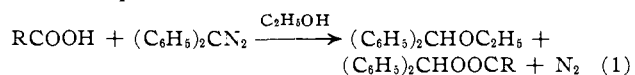
Medium Effects, Isotope Rate Factors, and the Mechanism of the Reaction of Diphenyldiazomethane with Carboxylic Acids in the Solvents Ethanol and Toluene¹

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It is proposed that the mechanism of the reaction of molecular acids (HA) with diphenyldiazomethane (DDM) in ethanol involves a slow proton transfer to give the ion pair $(C_6H_5)_2CHN_2^+A^-$. This is followed by the expulsion of nitrogen to give a second ion pair $(C_6H_5)_2CH^+A^-$ which may then either collapse to form ester or dissociate to form benzhydryl ethyl ether. This mechanism is consistent with the second-order kinetics, isotope effect $k_H/k_D = 3.5$ (benzoic-*h* acid in ethanol-*h* and benzoic-*d* acid in ethanol-*d*), and with an amount of ester in the product ($\alpha = 0.60-0.70$) which is essentially independent of the molecular acid or of deuterium substitution in it. Two factors, the polarity of the medium and the presence of more reactive acid dimers, account for medium effects on the slow step of the reaction of DDM with monomeric carboxylic acids. Thus, the second-order rate constant increases by a factor of 1.5 as the concentration of benzoic acid increases (0.0-0.7 *M*); addition of toluene causes the rate constant to drop from 0.69 (ethanol) to 0.42 (85 vol. % toluene) and then rise to 0.73 l. mole⁻¹ min.⁻¹ (toluene) at 27° . In toluene, the apparent second-order rate constant increases with benzoic-*h* and decreases with benzoic-*d* acid concentrations resulting in the peculiar divergence $k_H/k_D = 1.8-3.7$ (acid 0.015-0.25 *M*). It is believed that in toluene it is the dimer which is the reacting acid species and the relatively large concentration dependence is ascribed to a medium effect rather than to changes in acid association. Concerning the product-partitioning steps, it is believed that they are rapid and unselective or essentially diffusion controlled. However, specific "chemical factors," *i.e.*, the polarity of the medium, the nucleophilicity of the solvent, and the strength of added acids, compete with or alter the diffusion rates so that the ester to ether ratio in the products does change. The similarity to product-partitioning steps of solvolysis reactions is emphasized.

Certain reactions achieve a special importance. Next to pK values of acids, the rates of reaction of



acids with diphenyldiazomethane (DDM) are perhaps the most convenient measure of the effect of a substituent on reactivity. Thus, the literature contains examples from diverse acid families, *e.g.*, benzoic,²⁻⁶

phenylacetic,⁷ phenylpropionic,⁸ cinnamic,⁹ phenylpropionic,¹⁰ 2-furoic,¹¹ ferrocenic,¹² alkanolic,¹³ 4-cyclohexylcarboxylic,^{14,15} 4-bicyclo[2.2.2]octanecarboxylic,¹⁶ etc.¹⁷ Despite the extent of its application, aspects of the reaction mechanism remain unsettled.¹⁸ In the course of the present work, we found significant medium effects as well as results that bear on the mechanism in both ethanol and toluene. These are two solvents in which much of the previous work has been carried

(1) Acknowledgment is made to the U. S. Army Research Office, Durham, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 44T.

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