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The Non-planarity of 2-t-Butyl-3,7,7-trimethyltropilidene

BY KENNETH CONROW,[1] MERLIN E. H. HOWDEN AND DONALD DAVIS

A series of 2-substituted-3,7,7-trimethyltropilidenes, derived from eucarvone, has been prepared. The ultraviolet and nuclear magnetic resonance spectra have been used to identify each as a cycloheptatriene. The sterically demanding t-butyl group in the title compound permitted the observation that this molecule is non-planar and that there exists a barrier to inversion of the molecule through its average plane. The complexity of the vinyl hydrogen region of the n.m.r. spectra and the similarity of the n.m.r. spectra within the series of compounds suggest that all the tropilidenes are non-planar. No evidence was obtained for a valence tautomeric equilibrium.

One of us has already published certain observations which are relevant to the question of the intimate structure of molecules in the tropilidene series[2,3] and summarized the types of evidence which have been brought to bear on this problem.[3] Although part of this work[2] has now been shown to be wrong,[4] the suggestion that the intimate structure of tropilidenes is sensitive to the demands of the substituent group prompted a broader[5] investigation of 2-substituted tropilidene derivatives of eucarvone be made, with a view to determining their geometry and whether they are resonance hybrids (I ↔ II) or are mixtures of valence tautomers (I ⇌ II).

I   II
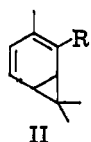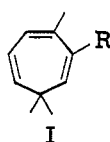
The essential point in distinguishing between a valence tautomeric mixture and a resonance hybrid is best made in terms of the energy profile of the molecule as the geometry (degree of planarity) of the molecular system is varied. If there is a single relative minimum in the profile, the system is a resonance hybrid. If there are two or more relative minima, the system is, in principle at least, a mixture of valence tautomers. This distinction between a resonance hybrid and a valence tautomeric mixture is independent of the question of the planarity or non-planarity of the molecule: the resonance hybrid might or might not be planar; the more nearly planar of the valence tautomers might or might not be planar. Further, resonance and valence tautomerism are not mutually exclusive: the two relatively stable geometries of a valence tautomeric system might each be described as a resonance hybrid, but the relative contribution of electronic structures I and II would differ for each tautomer.

Results.—With the foregoing considerations in mind, a series of 2-alkyl-3,7,7-trimethyltropilidenes were prepared by the action of alkylmagnesium halides on eucarvone. Additionally, the eucarvone enol esters of two sterically demanding carboxylic acids were prepared by the method of Corey and Burke.[6]

The ultraviolet spectra (Table I) of the hydrocarbon series show clearly the effect of the steric demand of the alkyl substituent. If the effect were electronic in na-

ture, one would expect each successive substitution of hydrogen by methyl to have a constant effect on the position of maximum absorption. In fact the series shows very little change up through the isopropyl derivative, whereupon a large effect is noted at the next addition of a methyl group to form the t-butyl group in a fashion characteristic of steric effects.

TABLE I
ULTRAVIOLET SPECTRA OF 2-R-3,7,7-TRIMETHYLTROPILIDENES (IN EtOH)

R	λ_{max}, mμ	log ϵ	λ_{min}, mμ	log ϵ
H	269	3.55	232	3.06
CH_3	268	3.59	234	3.08
C_2H_5	265	3.59	234	3.17
$i\text{-}C_3H_7$	265	3.58	235	3.21
$t\text{-}C_4H_9$	255	3.61	234	3.35
$(C_6H_5)_3CCOO$	267	3.66^a	252^a	3.58^a
$(C_6H_5)_2CHCOO$	269	3.61^a	244^a	3.39^a

^{a} The displacement of these values from those of the other members of the series is doubtless due to the presence of the phenyl nuclei in the substituent.

TABLE II
N.M.R. SPECTRA OF 2-R-3,7,7-TRIMETHYLTROPILIDENES

R	Vinyl H region	2-R^b	3-Me	7,7-Me$_2$
		—P.p.m. relative to tetramethylsilane as 10^a—		
H	3.77–5.09	..	8.05	9.05
CH_3	3.80–5.16	8.21	8.06	9.12
C_2H_5	3.79–5.35	7.82^c(9.11^c)	8.04	9.10
$i\text{-}C_3H_7$	3.82–5.62	7.54^c(9.08^c)	8.06	9.15
$t\text{-}C_4H_9$	3.78–5.01	(8.87)	7.87	9.06(8.76, 9.36^d)
$C_6H_5^f$	3.67–5.30	(2.96)	8.20	9.00
$(C_6H_5)_3CCO_2$	4.07–5.75	(2.88)	8.56	9.08
$(C_6H_5)_2CHCO_2$	3.74–5.42	(2.71^e)	8.44	9.08

^{a} These values were obtained by interpolation from audio-frequency side bands by different operators on different machines in different solvents and concentrations and probably contain errors up to ±0.1 p.p.m. ^{b} Values in parentheses are due to hydrogens of the substituent other than those alpha to the tropilidene nucleus. ^{c} Center of multiplet, J_{Et} 7.3 c.p.s.; $J_{i\text{-}Pr}$ 7.3 c.p.s. ^{d} Observed at ca. −100°. ^{e} The benzhydryl hydrogen is presumably obscured in the "vinyl hydrogen region." ^{f} Ref. 20.

TABLE III
VINYL HYDROGEN PATTERN IN THE N.M.R. SPECTRA OF 2-R-3,7,7-TRIMETHYLTROPILIDENES (τ-VALUES)^a

R	Group A	Group B	Group C
H	3.77–3.86	3.98–4.26	4.86–5.09
CH_3	3.80–3.90	4.10–4.36	4.99–5.16
C_2H_5	3.79–3.89	4.12–4.38	5.10–5.35
$i\text{-}C_3H_7$	3.82–3.94	4.14–4.39	5.37–5.62
$t\text{-}C_4H_9$	3.77–3.93	4.10–4.50	4.79–5.00

^{a} These values were determined in the 60 Mc. instrument by careful use of the audio side band technique and are probably accurate to ±0.02 p.p.m.

(1) Department of Chemistry, Kansas State University, Manhattan, Kan.

(2) K. Conrow, J. Am. Chem. Soc., 82, 5504 (1960).

(3) K. Conrow, ibid., 83, 2958 (1961).

(4) W. von E. Doering and M. R. Willcott, III, Tetrahedron Letters, No. 15, 663 (1962). We concur in the structural revision given.

(5) An earlier investigation by E. J. Corey, H. J. Burke and W. A. Remers, J. Am. Chem. Soc., 77, 4941 (1955), did not include sterically demanding substituents.

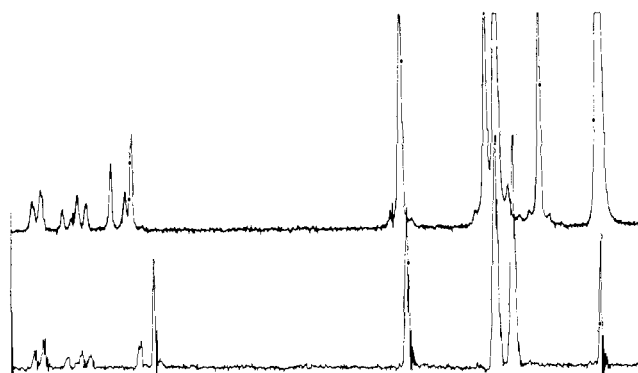(6) E. J. Corey and H. J. Burke, ibid., 78, 174 (1956).

Fig. 1.—The n.m.r. spectrum of 2-*t*-butyl-3,7,7-trimethylcyclo-heptatriene at two extremes of temperature: upper curve, at *ca.* −100° in carbon disulfide; lower curve, at +131° in carbon tetrachloride. The peak at the right is the tetramethylsilane standard.

The nuclear magnetic resonance (n.m.r.) spectra within this series showed very great similarity and the absorption characteristic of tropilidenes. There were no major changes in chemical shifts nor in the pattern in the vinyl hydrogen region. In view of the ultraviolet spectra, the *t*-butyl derivative was chosen for a more thorough investigation by the nuclear magnetic resonance technique. It turned out that the n.m.r. spectrum is insensitive to temperature above room temperature to 131°, but well below room temperature there is a gradual change in spectrum. In low temperature spectra (−100°, Fig. 1), the two methyl groups in the *gem*-dimethyl group are clearly distinct (separated by 0.6 p.p.m.) which indicates that they are non-equivalent. The room temperature spectrum differs from the low temperature spectrum most significantly in that in the former the two methyl peaks are coalesced into one of intermediate position. The spectra at intermediate temperatures (Fig. 2) show line broadening of the two methyl peaks as the temperature is raised, coalescence into a single broad peak at about −86° and then sharpening of this single peak as temperature is raised further toward room temperature.

An investigation of the temperature dependence of the n.m.r. spectra of each of the other hydrocarbons in the series gave no evidence of any change in the *gem*-dimethyl absorption down to *ca.* −100°.

The properties of the diphenylacetate and the triphenylacetate esters of eucarvone enol indicated that they exist in the cycloheptatriene form. Low temperature spectra gave no indication of change in the *gem*-dimethyl absorption for the triphenylacetate down to −90°. Examination of Fisher–Taylor–Hirschfelder models of eucarvone enol esters of other sterically hindered acids did not appear to offer significantly more steric hindrance than those reported here, and no further preparations along these lines were made.

Discussion and Conclusions.—The ultraviolet spectra of the compounds in the series of hydrocarbons clearly show the unusual nature of the *t*-butyl derivative. The other members of the series show ultraviolet absorption maxima at a position typical of simply substituted tropilidenes which have been amply demonstrated to exist in a cycloheptatriene form.[5] It is clear that substitution of a bulky alkyl substituent in the 2-position has been successful in modifying the intimate structure of the tropilidene rather markedly.

If this derivative existed as a mixture of valence tautomers, it would be expected that the ultraviolet spectrum would contain two overlapping maxima, one (*ca.* 273 mμ) due to excitation of molecules in the caradiene form and the other (*ca.* 265 mμ) due to excitation of

Fig. 2.—Temperature dependence of the *gem*-dimethyl resonance of 2-*t*-butyl-3,7,7-trimethylcycloheptatriene (in carbon disulfide with tetramethylsilane as internal standard). The peak at the right is due to the TMS, that at the left to the 3-methyl and the temperature-independent peak in the center is the *t*-butyl. Reading from top to bottom, the temperatures are −77°, −86°, −89° and −96°, respectively. The dotted portions have been added to show the probable appearance of the *gem*-dimethyl absorption where it is partially obscured by the *t*-butyl absorption.

molecules in the cycloheptatriene form. (According to the Franck–Condon principle, there is no question but that these forms would be distinguished by ultraviolet radiation.) In fact, the compound exhibits a single, nearly symmetrical absorption maximum at a position (255 mμ) well removed from that expected for either a caradiene or a cycloheptatriene. This observation appears to eliminate the possibility that the *t*-butyl hydrocarbon exists as a mixture of valence tautomers at room temperature[7,8] (unless, by some remote chance, both tautomers are distorted from their normal geometry to the degree necessary for them both to absorb near 255 mμ or one tautomer is of such high energy that it is present only to an insignificant extent in the mixture). The more reasonable conclusion, that the material is composed of a single markedly non-planar cycloheptatriene structure, found support in the n.m.r. spectrum of the compound, which, at room temperature, was in qualitative agreement with those of the lower homologs whose cycloheptatriene structure is established.[5] The observed separation of the absorption of the *gem*-dimethyl group into two peaks at low tempera-

(7) An ultraviolet spectrum was rather crudely determined at −70° (see Experimental) and appears to support the same conclusion at this lower temperature as well.

(8) This situation offers an interesting contrast to that obtaining in the case of 1,3,5-cyclooctatriene; A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

ture is accountable only if the molecule is non-planar. The behavior of this absorption with increasing temperature is indicative that the barrier to inversion of the molecule through its plane is rather low, the critical inversion temperature being about $-86°$. Unfortunately, the absorption of the t-butyl group right in the region of interest prevents the calculation of the magnitude of the inversion barrier.

These observations lead unequivocally to the conclusion that 2-t-butyl-3,7,7-trimethyltropilidene is non-planar in its ground state, but that the inversion of the molecule through its plane is rapid at ordinary temperatures. In the absence of evidence to the contrary, further discussion will assume the presence of a single resonance-hybrid structure.

Unfortunately, it has not yet proved possible to obtain compelling evidence that the less highly substituted tropilidenes and tropilidene itself are non-planar in their ground states, but rapidly inverting through the average plane of the molecule even at the lowest temperatures investigated. Nevertheless, certain arguments can be made which are believed to support this view.

First of all, it can be argued that the complexity and breadth of the n.m.r. spectra in the vinyl hydrogen region is indicative of non-planarity. Thus, in a non-planar structure the hydrogen atoms on C-1 and C-6 have a certain amount of cyclopropyl character due to the contribution of II to the resonance hybrid and thus absorb at higher field than the other hydrogens, in accord with the assignments which have been made.[9] The other hydrogens are also different from one another because the 2,5-hydrogens are disposed at different angles from the average plane of the ring than the 3,4-hydrogens and are different distances[10] from the center of circulation (if any) of the π-electrons around the ring.[11,12]

From the point of view that non-planarity of the ring system is to be associated with the complexity in the vinyl hydrogen region, the complexity of the spectra throughout the series, combined with the proven non-planarity of the t-butyl derivative, suggests that all the tropilidenes may be non-planar. Furthermore, the pattern of the resonances in the vinyl hydrogen region is very similar for each of the hydrocarbons reported here, though there are small differences in the spacing between each of the groups of absorption lines and in the total spread of the absorption in the region (see Table III). This parallelism further suggests the structural similarity through the series, i.e., that all are non-planar, though likely differing in the degree of non-planarity.[14]

(9) R. Bunton, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).

(10) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, **No. 19**, 839 (1962).

(11) The center of circulation (if any) of the π-electrons will *not* correspond to the center of gravity of the carbon atoms of the ring because C-7 is saturated and will not partake in the π-electron circulation.

(12) Two examples can be cited in support of the contention that planar, incompletely conjugated cyclic polyenes have narrow resonances in the vinyl hydrogen region of the n.m.r. spectra, namely, cyclopentadiene and 1,3-cyclohexadiene.[13] The narrowness of the vinyl hydrogen absorption is due, at least in part, to the "accidental" degeneracy of the vinyl protons. The argument made here is that the "accidental" degeneracy is due to the planarity of these molecules (perhaps by precluding the attainment of conformations in which the "different" hydrogens are differently shielded).

(13) W. Strohmeier, E. Lombard and R. M. Lemmon, *Z. Naturforsch.*, **14a**, 106 (1959); J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 847 (1957). Redetermination of these spectra under conditions of higher resolution show that cyclopentadiene has a complex multiplet about 20 cycles wide in the vinyl hydrogen region (G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960)) and that cyclohexadiene multiplet is about 5 cycles wide (this work) at 60 Mc.

(14) The notion that tropilidenes do not have a planar structure has been advanced by J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960), on the basis of the X-ray crystal structure determination of the molybdenum tricarbonyl, and by J. Gresser, A. Rajenbach and M. Swarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961), on the basis of the methyl affinity of tropilidene itself and shown by X-ray crystallography in one instance.[10]

An attempt to find a correlation between the spacing and/or the total spread of the vinyl hydrogen region and the steric demand of the substituent failed (see Table III). The changes (see Fig. 1) in the vinyl hydrogen region with temperature do not appear to offer any assistance in the assignment of structure to these molecules, but do suggest, at least, that certain modes of molecular motion are frozen out at lower temperature.[15]

The ultraviolet spectra, too, indicate that the tropilidenes are non-planar, though differing in the degree of non-planarity. If one makes an allowance of 5 mμ for the bathochromic effect of an alkyl substituent on an olefinic system and assumes that a substituent on the 7-position has no effect because it is not in conjugation, then the position of absorption of the triene chromophore "stripped" of the effect of substituents can be judged. (While these particular assumptions may be erroneous, the over-all argument will be unchanged, because there is no self-consistent set of values which will predict a constant λ_{max} for the triene chromophore.) If the degree of planarity of the triene were constant, the position of maximum absorption of the stripped chromophore would be constant. Since (see Table IV) there is considerable variation in the calculated values, it appears that the various tropilidenes vary in their degree of planarity. Only the most nearly planar of these could be planar; thus of the tropilidenes now known it would appear that only 1-methyl- and 3,7,7-trimethyl- could be planar and the others are non-planar according to this criterion. It may be noted that a prediction of the λ_{max} of a planar, conjugated, homocyclic triene according to Woodward's rule would give 293 mμ. The fact that the observed values are so much lower adds weight to the suggestion that these substances are all non-planar.

TABLE IV

Tropilidene	Observed, λ_{max}, mμ	Corrn. for substituents	λ_{max} of "stripped" chromophore, mμ
Unsubstd.	261[a]	..	261
7-CH$_3$	257[b]	..	257
1-CH$_3$	269[c]	-5	264
2-CH$_3$	258[c]	-5	253
3-CH$_3$	260[c]	-5	255
3,7,7-(CH$_3$)$_3$	269[d]	-5	264
2,3,7,7-(CH$_3$)$_4$	268[d]	-10	258
2-C$_2$H$_5$-3,7,7-(CH$_3$)$_3$	265[d]	-10	255
2-i-C$_3$H$_7$-3,7,7-(CH$_3$)$_3$	265[d]	-10	255
2-t-C$_4$H$_9$-3,7,7-(CH$_3$)$_3$	255[d]	-10	245

[a] W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957). [b] K. Conrow, *ibid.*, **83**, 2343 (1961). [c] N. H. Nelson, J. H. Fassnacht and J. V. Piper, *ibid.*, **83**, 2206 (1961); **81**, 5009 (1959). [d] This work.

Theoretically, both relief in the bond angle compression strain involved in a totally planar ring and the increase in 1,6-overlap energy by inclusion of σ-character in the 1,6-overlap[16] favor the non-planar form. Only the small decrease in π-overlap of adjacent p-orbitals at C-2, C-3 and at C-4, C-5 would tend to disfavor the non-planar form.

The failure of the two eucarvone enol esters to show modified properties is probably due to a decrease in the effective steric demand of the bulky group on account of its having been removed by one more bond distance and one more rotatable bond from the position where steric demand is effective.

The Experimental section records the details of certain experiments briefly reported earlier[3] on the estimation of the 1,6-overlap energy in these tropilidenes.

(15) J. A. Pople, *Mol. Phys.*, **1**, 3 (1958).

(16) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).
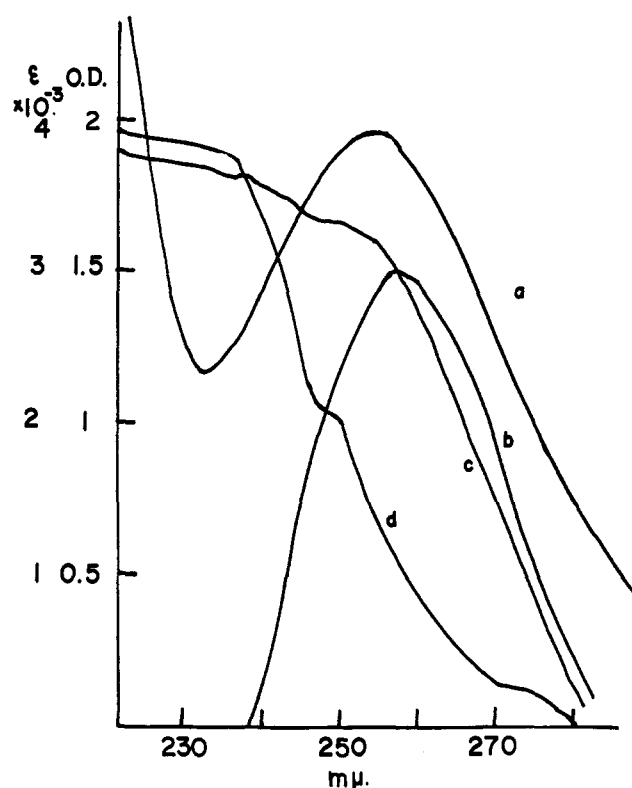
Fig. 3.—Ultraviolet spectra of 2-t-butyl-3,7,7-trimethyl-tropilidene: a, in 95% ethanol at room temperature; b, in 2,2,4-trimethylpentane at −70° obtained by difference between; c, the absorption curve of sample, solvent and refrigerant; d, the absorption curve of solvent and refrigerant. Curves a and b have molar absorption coefficient (ε) as the ordinate and curves c and d the optical density as the ordinate.

Experimental

Melting points were taken in capillary tubes and are corrected; boiling points are uncorrected. Infrared and ultraviolet spectra were determined by Miss Donna Karasek, Miss Karen Darnell and Mr. Don Steele on Cary models 11 or 14 or on a Perkin-Elmer model 21. Microanalyses were done by Miss Heather King. The n.m.r. spectrometers used were a Varian V-4300B with superstabilizer operating at 40 Mc. and a Varian V-4300B with superstabilizer operating at 60 Mc. In the preparations of the various substituted tropilidenes for investigation of their spectral properties no special effort was made to optimize the yields obtained. In several cases, one run served to produce the required amount of material.

3,7,7-Trimethylcycloheptatriene-1,3,5 (I, R = H) was prepared by the method of Corey, Burke and Remers[17] and given a final purification by preparative v.p.c. in a 0.75 in. i.d. 1-m. didecyl phthalate column at 125°; n^{25}D 1.4955.

2,3,7,7-Tetramethylcycloheptatriene-1,3,5 (I, R = Me) was prepared by the method of Rupe and Kerkovious.[18] The mixture[3] of the cycloheptatriene and the methylenecycloheptadiene was resolved by preparative v.p.c. on the didecyl phthalate column at 125°. The first major peak, n^{25}D 1.5010, was identified as the cycloheptatriene on the basis of its infrared, ultraviolet and n.m.r spectra.[3]

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.00; H, 10.95.

2-Methylene-3,7,7-trimethyl-3,5-cycloheptadiene, n^{25}D 1.5178, was eluted next and was identified on the basis of its infrared, ultraviolet and n.m.r. spectra.[3]

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.25; H, 10.89.

2-Ethyl-3,7,7-trimethylcycloheptatriene-1,3,5 (I, R = Et) was prepared by the appropriate modification of the method of Rupe and Kerkovious[18] by the addition of 7.5 g. (50 mmoles) of eucarvone to a solution of ethylmagnesium bromide at room temperature prepared from 1.80 g. of magnesium (75 mg.-atoms) and 8.70 g. of ethyl bromide (80 mmoles) in a total of 75 ml. of dry ether. The solution was poured into ice and ammonium chloride solution,

washed with 5% sodium bicarbonate solution, dried, concentrated and distilled at about 68° (0.8 mm.). An infrared spectrum of the material showed considerable ketonic material (ν^{neat}_{max} 1700 cm.$^{-1}$) indicating that conjugate, as well as 1,2-, addition had occurred. The entire mixture was subjected to dehydration conditions[19] by distilling from a bit of potassium bisulfate at 70–110° (20–10 mm.). The distillate was redistilled and the material collected at 68–84° (6 mm.) given a purification by preparative v.p.c. on the didecyl phthalate column at 145°. There was collected 0.71 g. (4.4 mmoles, 9%) of oil, n^{25}D 1.4968, after redistillation at 80° (8 mm.).

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.23.

2-Isopropyl-3,7,7-trimethylcycloheptatriene-1,3,5 (I, R = i-Pr) was prepared as above, except that the addition of the eucarvone (50 mmoles) to the isopropylmagnesium bromide solution (prepared from 75 mg.-atoms of magnesium and 80 mmoles of isopropyl bromide in a total of 40 ml. of dry ether) was done at −70°. An infrared spectrum of the crude adduct showed that only a very minor proportion of the addition had occurred in the desired 1,2-fashion. The mixture was subjected to dehydration by distillation[17] from a bit of p-toluenesulfonic acid and material distilling at 78–103° (16 mm.) was collected. This distillate was further purified by preparative v.p.c. on a 0.75 in. i.d. 1-m. γ-methyl-γ-nitropimelonitrile column at 105°. The first major fraction was collected and redistilled at 94° (17 mm.), n^{25}D 1.4904, and amounted to 0.18 g. (2%).

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.75; H, 11.64.

The second major fraction from the v.p.c. amounted to 0.09 g. (1%), was redistilled at 104° (19 mm.), n^{25}D 1.4932, and appeared to be 2,4-diisopropyltoluene (lit.[20] b.p. 104–108° (18 mm.), n^{20}D 1.4912, 1.4946) on the basis of infrared absorption characteristic of aromatic substances at 732, 755, 817, 888, 1500 and 1610 cm.$^{-1}$. This substance would arise by ring contraction of the cycloheptatriene under the acidic dehydration conditions (cf. ref. 3).

2-t-Butyl-3,7,7-trimethylcycloheptatriene-1,3,5 (I, R = t-Bu) was prepared as above by the slow addition of 8.9 g. of eucarvone to a cooled (−70°) solution of t-butylmagnesium chloride prepared[21] from 0.1 mole of t-butyl chloride and 0.1 g.-atom of magnesium in a total of about 40 ml. of dry ether. The adduct was distilled, after a standard work-up, at about 100° (1.7 mm.) and showed weak hydroxyl absorption. The mixture was subjected to dehydration conditions by distillation over p-toluene-sulfonic acid. The distillate collected from 84–100° (5 mm.) was finally purified by preparative v.p.c. on the nitromethylpimelonitrile column at 130°. The first major fraction eluted was collected and redistilled at 95–96° (12 mm.) and amounted to 0.51 g. (4.5% yield), $n^{24.5}$D 1.4931.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.04; H, 11.55.

The ultraviolet spectrum of 2-t-butyl-3,7,7-trimethyltropilidene was also obtained at ca. −70° in a 1-cm. quartz cell immersed in a solid CO_2-ethanol mixture in a double-quartz-windowed dewar flask.[22] Considerable difficulty was experienced in obtaining good spectra due to the absorption and light scattering effect of the bubbling refrigerant. Nevertheless, a crude spectrum was obtained by subtracting the absorption of the solvent (2,2,4-tri-methylpentane) taken under identical conditions in the cold apparatus from that of the solution. The absorption so measured (λ_{max} 257.5 mμ, log ε 3.48) is not believed to differ appreciably from that at room temperature (λ_{max} 254 mμ, log ε 3.61) in view of the experimental difficulties involved (see Fig. 3). In any case there was no evidence of the hyperchromic shift to be expected if the molecule became more caradiene-like at lower temperature (as the n.m.r. spectrum might be taken to suggest), nor was there any evidence of two absorption peaks as would be the case if there were two valence tautomers present at lower temperature.

The infrared spectra of the series of hydrocarbons reported here (R = H, Me, Et, i-Pr, t-Bu) showed a very marked similarity. Aside from the peaks expected of hydrocarbons of this structure near 2900, 1610–1625, 1450 and 1375 and 1360 (gem-dimethyl), they absorbed in common in the regions 1550–1555 (weak, broad), 1190–1215 (medium, sometimes a doublet), 1139–1150 (medium), 835–858 (medium-strong), 812–822 (medium), 740–766 (strong) and 702–716 (strong). The latter two bands correspond to those reported earlier[23] in the spectra of 7-

(17) E. J. Corey, H. J. Burke and W. A. Remers, *J. Am. Chem. Soc.*, **78**, 180 (1956).

(18) H. Rupe and W. Kerkovious, *Ber.*, **44**, 2702 (1911).

(19) K. Alder, K. Kaiser and M. Schumacher, *Ann.*, **602**, 80 (1957).

(20) H. Pines, A. Weizman and V. N. Ipatieff, *J. Am. Chem. Soc.*, **70**, 3859 (1948); V. Sijkora, V. Herout, J. Pliva and F. Sorm, *Collection Czech. Chem. Commun.*, **19**, 124 (1954).

(21) F. C. Whitmore and A. L. Houk, *J. Am. Chem. Soc.*, **54**, 3714 (1932).

(22) The authors thank Edward Erath of the Hughes Research Division for his coöperation in making this measurement.

(23) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

monosubstituted tropilidenes, but the band in the 1358–1410 region reported in the earlier series is lacking in these. The present series of compounds do not absorb at 1500 and 1600 cm.$^{-1}$, indicating freedom from aromatic impurity; the only region in which the spectra differ markedly from one another is between 900 and 1100 cm.$^{-1}$.

Eucarvone enol triphenylacetate (I, R = triphenylacetoxy-) was prepared by the method of Corey and Burke[24] from 9.95 g. (32.4 mmoles) of triphenylacetyl chloride[25] and sodio-eucarvone prepared from 1.27 g. (32.4 mmoles) of sodamide and 4.45 g. (29.8 mmoles) of eucarvone in 50 ml. of dioxane. The reaction mixture was treated with Celite and filtered through Celite, concentrated *in vacuo*, and the residue taken up in hot 95% ethanol. There was isolated by fractional crystallization 2.60 g. of light yellow needles, m.p. 95–99°. Chromatography of the solids from the mother liquors of this material gave, from the pentane eluates, an additional 0.30 g. of nearly colorless needles after one additional crystallization from absolute ethanol; m.p. 100.5–102.0°, total yield 23%.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.44; H, 6.63.

Eucarvone Enol diphenylacetate (I, R = Diphenylacetoxy-).—The above procedure, using diphenylacetyl chloride,[26] gave rise to a total of a 39% yield of crude yellow crystals, m.p. 70–77°. A portion of this, after chromatography on alumina and crystallization from 95% ethanol, gave nearly colorless needles, m.p. 79.0–81.0°.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.12. Found: C, 83.69; H, 7.12.

Isomerization of 2,3,7,7-Tetramethylcycloheptatriene-1,3,5 to 4-Isopropyl-o-xylene. Preparative Run.—A solution of 0.80 g. of p-toluenesulfonic acid and 0.50 ml. of the tetramethyltropilidene in 17.0 ml. of glacial acetic acid was allowed to stand at room temperature 17 hours. Pentane and water were added, the water layer discarded and the pentane layer washed with water and bicarbonate solution. Preparative v.p.c. of the concentrated pentane layer on the didecyl phthalate column at 125° afforded a single symmetrical peak which was collected and redistilled at 102° (20 mm.), n^{25}D 1.4972 (lit.[27] $n^{15.5}$D 1.50001, n^{20}D

1.5010). The substance showed infrared absorption appropriate for 4-isopropyl-o-xylene: 815 (appropriate for two adjacent H's), 875 (appropriate for one H), 1503, 1611, 3010sh (aromatic absorption) and broad weak bands near 1745 and 1870 cm.$^{-1}$ (appropriate for a 1,2,4-substituted benzene). Nitric acid oxidation[28] gave material, m.p. 164.5–166.0°, 3,4-xylic acid, as expected for the compound with the assigned structure. When this isomerization was attempted in solutions more concentrated in the tropilidene component, considerable proportions of higher boiling materials, presumably olefin dimerization products, were formed.

Kinetic Runs.—A solution of 1.1926 g. of p-toluenesulfonic acid hydrate in 25.00 ml. of commercial glacial acetic acid was prepared. Two 5.00-ml. aliquots were transferred to nitrogen-swept serum-capped vials and equilibrated at 25.0° before 137.1 mg. (0.925 mmole) of 2-methylene-3,7,7-trimethylcycloheptadiene-3,5 and 132.5 mg. (0.894 mmole) of 2,3,7,7-tetramethylcycloheptatriene-1,3,5 were introduced into the respective vials by means of a hypodermic syringe. Aliquots (0.33 ml.) were withdrawn from time to time by means of the hypodermic syringe, added to 1.0 ml. of pentane and washed with two portions of water and one of bicarbonate solution. A 0.15-ml. aliquot of the pentane solution served for the v.p.c. sample for a didecyl phthalate column at 125°. The sum of the areas of the three peaks due to the tropilidene, the methylene cycloheptadiene and the o-xylene (listed in order of elution) was normalized to 100 and log (100 – area o-xylene) was plotted against *t*, measured from the instant of injection of the hydrocarbon samples. The lines obtained in this way (a slight downward curvature and a slight S-curvature appeared, respectively) corresponded to pseudo-first-order rates of 1.07 and 1.14 × 10^{-4} sec.$^{-1}$ (±10%), respectively. The ratio of the areas of the peaks due to the methylene cycloheptadiene and to the tropilidene was determined for each point; this ratio became increasingly uncertain as the areas of the peaks concerned became smaller as the reaction proceeded. During the first half-life of the reactions, the values of the ratio became 12:88 and 8:92, respectively.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES, SYDNEY, AUSTRALIA]

The Ionization Constants of N-(Substituted-phenyl)-glycines

BY A. BRYSON, N. R. DAVIES AND E. P. SERJEANT[1]

The ionization constants of ten N-(substituted-phenyl)-glycines, $RC_6H_4NHCH_2COOH$, and their corresponding ethyl esters have been measured, the substituent R being varied throughout the series H, m-NO$_2$, m-CN, m-Cl, m-COCH$_3$, p-Cl, m-OMe, m-Me, p-Me and p-OMe. These values have been used in conjunction with spectral data to calculate the zwitterion equilibrium constants and the constants pertaining to the individual ionization processes. The results invalidate Wegscheider's assumption that the pK_a value of the non-zwitterionic acid pK_B can be equated to the pK_E of the ethyl ester, the expression $pK_B = pK_E + 0.20$ being obtained for the ten substituents. The relations between the individual ionization constants and the zwitterion equilibrium constant lead to inter-related Hammett equations which are compared with the equations applying to m-substituted anilines and the phenylglycine esters on one hand and with m-substituted phenylpropionic acids on the other. A relation is derived between zwitterion ratios and substituent constants.

As part of a program to determine the relation between the biological activity of N-(substituted-phenyl)-glycines and their metal binding properties it was necessary to determine the effects of ring substituents on the ionizations of the two functional groups in their side chains. This paper records the ionization constants and the ultraviolet absorption spectra of ten of these compounds and their ethyl esters. Interpretation of the experimental pK_a values is complicated by the presence of the zwitterion equilibrium

$$RC_6H_4NHCH_2CO_2H \rightleftharpoons RC_6H_4NH_2{}^+CH_2CO_2{}^-$$
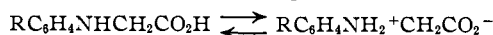
established because of the proximity of the pK_a values of the anilinium and carboxyl groups. The fortuitous choice of the predominantly non-zwitterionic N-(m-nitrophenyl)-glycine as the first compound to be in-

vestigated revealed that pK_1, the experimental ionization exponent of the reaction

$$m\text{-}NO_2C_6H_4\overset{+}{N}H_2CH_2CO_2H \rightleftharpoons m\text{-}NO_2C_6H_4NHCH_2CO_2H + H^+$$

was greater than pK_E for the corresponding ethyl ester. This behavior was subsequently confirmed when the constants for the substituents m-CN, m-Cl, m-COMe and p-Cl were obtained. These findings are in conflict with the Ebert–Wegscheider assumption[2] that the effect of a carboxy group can be equated with that of a carboethoxy or carbomethoxy group. This assumption has been widely used[3] in evaluating the zwitterion constants K_Z and the individual ionization exponents pK_A, pK_B, pK_C and pK_D for reactions of the type in eq. 1–4.

(1) Royal Military College, Duntroon, A.C.T., Australia.

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