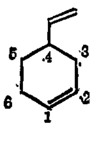
Reactions of Free Radicals with Olefins. Dehydro Dimer Structures of 4-Vinylcyclohexene

J. REID SHELTON AND JEROME F. SIUDA[1]

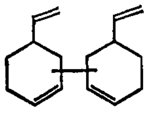
Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

Received August 20, 1965

Prior studies[2-4] have shown that *t*-butoxy radicals react with 4-vinylcyclohexene (I) primarily *via* hydrogen abstraction rather than by addition to either of the available double bonds. Elemental analysis, infrared spectra, and hydrogenation of the major reaction product were consistent with formation of a dehydro dimer type of structure (II) by coupling of vinylcyclohexenyl free radicals.



I



II

This study was undertaken to establish whether or not dehydro dimers of this type are formed, and to determine the relative proportions of isomers of structure II obtained from the reaction.

The reaction was carried out by ultraviolet photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene (80°). After removal of *t*-butyl alcohol and excess 4-vinylcyclohexene by distillation at reduced pressure, the dehydro dimer fraction was collected. Vapor phase chromatography showed evidence of one major type of product with a retention time of 21 min on a 12 × 0.25 in. silicone grease column, plus minor components at 18.5 and 26 min (as shown in Figure 1). The yield of these dimeric products by vapor phase chromatography was 44% based on *t*-butyl alcohol produced.

Walling and Thaler[5] have determined the relative reactivities of allylic hydrogens toward *t*-butoxy radical in the reaction of *t*-butyl hypochlorite with a number of model compounds. Applying their values to the case of 4-vinylcyclohexene predicts 88% attack on the secondary allylic hydrogens in the 3- and 6-positions, *ca.* 10% attack at the tertiary allylic hydrogen in the 4-position, and 2% attack on the unactivated methylene hydrogens in the 5-position. The model compound used for their tertiary allylic hydrogen reactivity was open chain, and thus may not be directly applicable to 4-vinylcyclohexene. However, Farrissey[6] has shown that a tertiary allylic hydrogen is more reactive than secondary only when the tertiary C–H and the adjacent double bond are part of the same ring.

Experimental evidence[2,4] indicates little hydrogen abstraction by *t*-butoxy radical occurs at the 4-position of 4-vinylcyclohexene. This lower reactivity may be due to a steric effect of the vinyl group which hinders attack by the bulky *t*-butoxy radical at both the 3- and 4-positions. The 6-position would then be most available for free radical formation (IIIa), consistent with the observation that reaction at the 6-position is much more extensive than at the 3-position.[2] When hydrogen abstraction does occur at the 3-position, the resulting free radical will have two nonequivalent resonance forms, IIIb and c. Subsequent coupling of radicals would be less hindered with the electron localized as in IIIc rather than on the carbon from which the hydrogen was abstracted (IIIb).

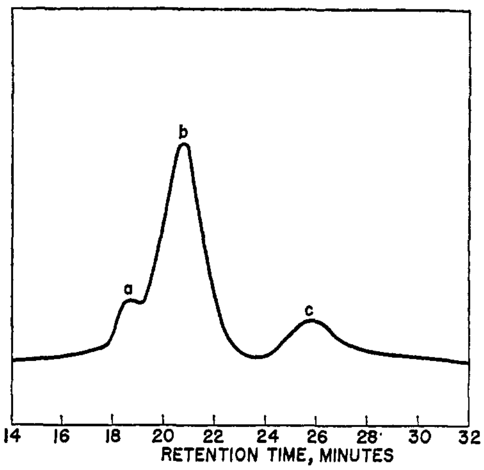
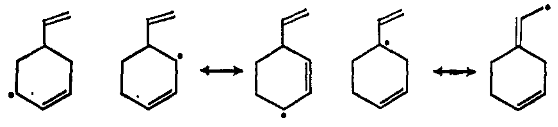


Figure 1.—Vapor phase chromatogram of dehydro dimer fraction.



IIIa IIIb IIIc IIId IIIe

With the above reasoning and experimental evidence the availability of isomeric vinylcyclohexenyl radicals for coupling should be in the order: IIIa >> IIIc > IIIb >> IIIe > IIId. Neglecting the possible products derived from hydrogen abstraction at the tertiary position, one can predict a relative abundance of the other dehydro dimer structural isomers expected to be present in the reaction product: IIa,a >> IIa,c > IIa,b >> IIc,c > IIb,c > IIb,b.

Because the synthesis and subsequent identification of the various isomeric dehydro dimer structures posed a difficult problem, it was thought that identification could be accomplished more readily by aromatization of the dehydro dimer followed by comparison with known biphenyl compounds. Aromatization of the dehydro dimer fraction was accomplished with palladium–charcoal as a dehydrogenating agent. Vapor phase chromatography on the reaction mixture gave eight peaks as indicated in Figure 2 and described in Table I.

Authentic samples of the six isomeric diethylbiphenyls were prepared and used for peak enrichment studies and for comparison of infrared and ultraviolet spectra. Peaks 1, 3, 4, and 6–8 were identified by these methods as corresponding to 2,2′-, 2,3′-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-diethylbiphenyl. The relative amounts of these isomers as estimated from the peak areas are reported in Table I. The observed order is 3,3′- >> 3,4′- ≈ 2,3′- >> 2,4′- > 4,4′- >> 2,2′- which is quite similar to the predicted sequence. The only

---

[1] Participant, summer 1964, National Science Foundation Research Participation for College Teachers Program.

[2] J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, **26**, 2185 (1961).

[3] J. R. Shelton and A. Champ, *ibid.*, **28**, 1393 (1963).

[4] J. R. Shelton and H. G. Gilde, *ibid.*, **29**, 482 (1964).

[5] C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

[6] W. J. Farrissey, Jr., *J. Org. Chem.*, **29**, 391 (1964).

TABLE I[a]

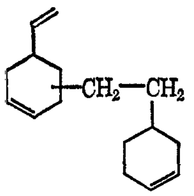
DIETHYLBIPHENYLS OBSERVED IN REACTION MIXTURE OF AROMATIZED DEHYDRO DIMER

Vpc peak	Retention time,[b] min	Rel peak area	Diethyl-biphenyl	Major infrared bands[c]	Ultraviolet max,[d,e] mμ
1	16.5	1	2,2′-	1010, 750	261 (263.5)[e] 269 (271)
3	20	20	2,3′-	900, 800, 755, 715	236
4	21.5	4	2,4′-	1010, 840, 765	236
6	30.5	30	3,3′-	890, 795, 710	249 (251)[d]
7	33	20	3,4′-	890, 830, 795, 705	253
8	35	8	4,4′-	1010, 820	256 (256)[d]

[a] The infrared and ultraviolet data are described for the diethylbiphenyls prepared by the Ullmann reactions. Identification of the vpc peaks were made by comparison. [b] Retention times are taken from the acme of each peak. [c] Carbon disulfide solutions. [d] 95% ethanol. [e] Values in parentheses are literature values.

reversal of the predicted order involves the poorly resolved peak 4. Thus, all six of the possible dehydro dimers that could be formed by coupling of the isomeric vinylcyclohexenyl radicals derived from abstraction of the secondary allylic hydrogens of 4-vinylcyclohexene by *t*-butoxy radicals are actually present in the dehydro dimer product in the relative proportions expected if attack at the least hindered of these two positions is favored.

Peaks 2 and 5 have not been definitely characterized; however, comparison of retention times, and peak enrichment with the unaromatized dehydro dimer fraction, indicates that peaks 2 and 5 correspond to two minor peaks, one just preceding and the other following the one large peak, in the chromatogram of the original reaction product. Evidence is presented in another paper of this series[7] that vinylcyclohexenyl radicals may also add to the vinyl double bond, and subsequent abstraction of hydrogen could produce dimers of the type shown. These and any dehydro



dimers formed by coupling of radicals resulting from abstraction of the tertiary allylic hydrogen, and localized as in IIId and IIIe, would not aromatize to biphenyl derivatives, and thus would persist either in the original form or as a dehydrogenated product in the aromatized reaction mixture.

All of the diethylbiphenyl compounds employed in this investigation were prepared from the appropriate iodoethylbenzenes by the Ullmann reaction. The *m*- and *p*-ethyliodobenzenes were made by diazotization of the corresponding amino compounds followed by treatment with potassium iodide; *o*-ethyliodobenzene is commercially available.

The symmetrical diethylbiphenyls have been well characterized;[8] thus only the preparations of the three unsymmetrical diethylbiphenyls heretofore not reported in the literature are described here.

Experimental Section

Photolysis of Di-*t*-butyl Peroxide in 4-Vinylcyclohexene.—The apparatus and reagents have been described in a previous paper.[3] 4-Vinylcyclohexene (165 g, 1.5 moles) and di-*t*-butyl peroxide (36 g, 0.25 mole) were heated at 80° in the presence of an ultraviolet light source for 3 days after which time both the *t*-butyl alcohol and excess 4-vinylcyclohexene were removed by distillation at reduced pressure. Careful distillation of the residue [bp 78–81° (0.05–0.07 mm)] on a 6-in. glass column afforded dehydro dimer mixture. Formation of polymeric substances was inevitable on prolonged distillation. Analysis of the dehydro dimer by vapor phase chromatography (vpc) showed one large peak with smaller peaks immediately preceding and following. Infrared spectra of the dehydro dimer showed vinyl and *cis* internal unsaturation as previously reported.[3]

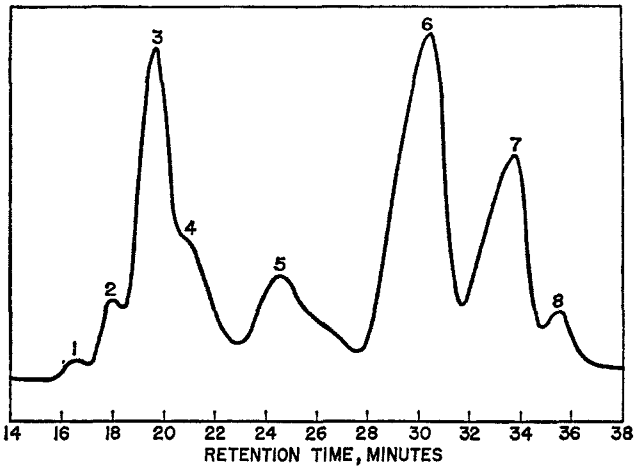


Figure 2.—Vapor phase chromatogram of the reaction mixture of aromatized dehydro dimer.

Aromatization of Dehydro Dimer.—A 25-ml round bottom flask equipped with a reflux condenser, a nitrogen inlet, and a magnetic stirring bar was heated to *ca.* 250° while flushing the system with nitrogen for 1 hr. To the flask was added 5% palladium–charcoal[9] (0.5 g) followed by careful dropwise addition of freshly distilled dehydro dimer (5.0 g, 0.023 mole). An exothermic reaction ensued but could be controlled by the mode of addition of reagent. The mixture was stirred at 250° for 10 hr under a nitrogen atmosphere, then cooled, and the liquid phase was diluted to 10 ml with benzene. The palladium–charcoal was filtered and washed with boiling benzene (5 × 5 ml). Distillation removed the solvent and the clear liquid residue was subjected to vpc analysis. Eight peaks appeared in the chromatogram. Further characterization is described in Table I. Peaks 2 and 5 with retention times of 18 and 24.5 min, respectively, correspond closely to the minor components in the chromatogram of the dehydro dimer mixture.

Preparation of the Isomeric Diethylbiphenyls.—Generally, activated copper[10] was heated with an equal weight of the iodo compound(s) at 250° for 4–6 hr. Purification by distillation of

---

(7) J. R. Shelton and A. E. Champ, *J. Org. Chem.*, **30**, 4183 (1965).

(8) P. M. Everitt, D. M. Hall, and E. E. Turner, *J. Chem. Soc.*, 2286 (1956).

(9) Lot No. 6861. Engelhard Industries, Newark 2, N. J. Aromatization reactions with palladium–charcoal catalyst at comparable temperatures have been shown to form expected products without rearrangement: E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

(10) Copper metal powder, 150 mesh (E. H. Sargent and Co., Chicago, Ill.) activated by the Adam's method: E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4219 (1933).

the diethylbiphenyls was not attempted. However, the coupling products seem to have been prepared in very good yield based on vpc of the reaction mixture.

The preparation of 3,4′-diethylbiphenyl is described as a typical reaction. 3-Ethyliodobenzene (4.5 g, 0.019 mole) and 4-ethyliodobenzene (4.5 g, 0.019 mole) were added to a test tube (25 × 200 mm) maintained at *ca.* 200°. Activated copper (9.4 g) was added in portions over a 1-hr period. The reaction mixture was then heated for 4 hr (total, 5 hr) at about 250° and stirred occasionally with a thermometer. After cooling, the reaction mixture was extracted with boiling benzene (6 × 20 ml). Most of the benzene was then removed by distillation leaving a clear, yellow liquid. Vpc showed three major peaks, two of which were identified as the 3,3′ and 4,4′ isomers. The remaining peak was thus the 3,4′ isomer; hence it was trapped and analyzed. The infrared spectra (Table I) showed absorptions characteristic of both *meta* and *para* aromatic substitution.

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.47; H, 8.67.

By analogous procedures the 2,4′ and the 2,3′ isomers were prepared and characterized.

Anal. Found for 2,3′-diethylbiphenyl: C, 91.53; H, 8.41. Found for 2,4′-diethylbiphenyl: C, 91.57; H, 8.48.

Infrared spectra were obtained on a Perkin-Elmer Model 237B spectrophotometer. A Beckman DB was employed in the ultraviolet analyses. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. A 12 ft × 0.25 in. silicone grease column was used for all of the gas chromatography investigations at the following conditions: column, 250°; injection port, 325°; detector, 345°; helium flow, 75 cc/min; pressure, 30 psi; bridge current, 125 ma.

Cycloaddition of Dimethylketene to Olefinic Substrates

A. Paul Krapcho and Joseph H. Lesser

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

Received February 28, 1966

The recent report on the addition of ketenes to dienes and olefins prompts us to report our results from a similar study.[1] This paper describes the addition of dimethylketene to several olefinic substrates to produce good yields of the corresponding 1,2-cycloaddition products.

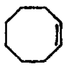
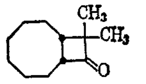
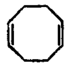
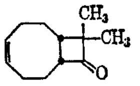
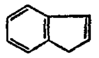
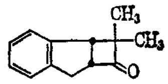
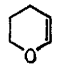
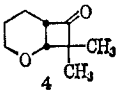
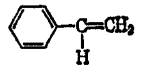
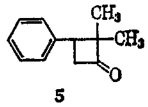
The reactions of ketene or disubstituted ketenes with sufficiently activated double bonds such as conjugated dienes,[1] vinyl ethers,[2] and enamines[3] proceed readily and generally in good yields. Simple olefinic substrates undergo a slower reaction with ketenes in which the dimerization of the ketene competes with the cycloaddition. Bestian and Günther[4] reported that the thermal decomposition of the acylal of dimethylketene in the presence of olefins at elevated temperatures leads to good yields of the 1,2-cycloadducts of dimethylketene with simple acyclic olefins and cyclohexene. Cyclic olefins such as cyclohexene, cyclooctene, and 1,5-cyclooctadiene have entered into cycloadditions with butylethylketene.[1]

Because of the accessibility of tetramethyl-1,3-cyclobutanedione (commercially inexpensive) and its known thermal decomposition into dimethylketene, it was chosen as the source material for this study of the addition of dimethylketene to several types of olefinic substrates. A modified ketene generator[5] was utilized to generate the dimethylketene from its dimer. The dimethylketene was carried by the nitrogen flow into the olefin which was heated in an oil bath. The mixture was then allowed to react overnight. The unreacted olefin was recovered by distillation and the adduct was either distilled or crystallized.

In this manner the reactions of dimethylketene with cyclooctene, 1,5-cyclooctadiene, styrene, indene, and dihydropyran were performed. In the latter three cases, the addition could yield different isomers depending on the direction of addition to the double bond. However, only one isomer was formed and the structural assignments of the products were ascertained by infrared, nmr, and deuterium exchange experiments. The results of this study are tabulated in Table I.

Table I

Dimethylketene–Olefin Adducts and Yields

Olefin[a]	Product structure		% yield
	 1		77[b]
	 2		55[b]
	 3	[d]	64[b]
		[e]	42[c]
	 5		20[c]

[a] In all runs a 3–5 *M* excess of olefin to starting dimer was utilized. [b] Yield based on unrecovered olefin. [c] Yield based on dimer, assuming a quantitative conversion to monomer. [d] The formation of this adduct is reported in ref 1 in a 12% yield using hexane as the solvent. No structural evidence was presented. [e] Previously reported in ref 2a in a 73% yield using ether as the solvent. No structural evidence was presented.

The nmr spectra for **1** and **2** are listed in the Experimental Section. The structure of the indene–dimethylketene adduct was established as **3** by the nmr spectrum (solution in carbon tetrachloride) which showed a 1 H doublet of triplets at 4.0 ppm for the tertiary hydrogen adjacent to the carbonyl group,[1,6] a 3 H singlet at 0.7 and a 3 H singlet at 1.37 ppm for the dissimilar methyl groups, a 3 H multiplet pattern spread over 2.6–3.7 ppm for the benzylic hydrogens (this pattern showed two unsymmetrical doublets centered at 3.0 for 2 H and 3.6 ppm for 1 H along with

---

(1) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

(2) (a) R. H. Hasek, P. G. Gott, and J. C. Martin, *ibid.*, **29**, 1239 (1964), and references cited therein; (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *ibid.*, **30**, 4309 (1965); (c) R. Husigen, L. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

(3) G. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., *J. Org. Chem.*, **30**, 2642 (1965), and references cited therein.

(4) H. Bestian and D. Günther, *Angew. Chem. Intern. Ed. Engl.*, **2**, 612 (1963).

(5) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

(6) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 487 (1964).