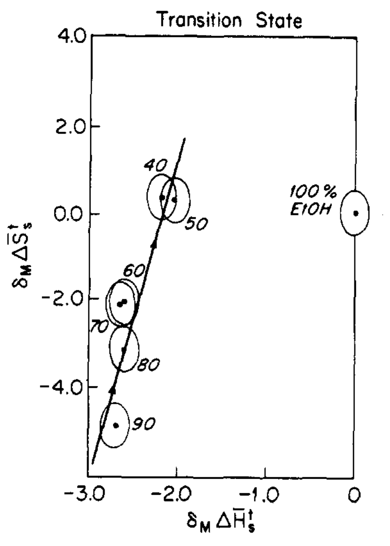


Figure 3. Isokinetic plot for solvation of *t*-butyl chloride transition state in aqueous ethanol solution.

simple linear behavior, the striking exception to which is the point for pure ethanol. Of particular importance is the fact that the points in Figure 3 follow a rational order[5] (indicating that their arrangement along the line is probably in response to a genuine physical effect and not just experimental errors) and that the $\delta_M\Delta H/\delta_M\Delta S$ slope of this line (0.14) is nearly the same (0.15) as may be found for several simple salts in a similar series of aqueous methanol solutions as calculated from the data of Latimer and Slansky.[13]

The fact that the 100% ethanol point for the *t*-butyl chloride transition state is displaced from its $\delta_M\Delta\bar{H}_s$ *vs.* $\delta_M\Delta\bar{S}_s$ line, while the corresponding point for the simple salts is not, suggests strongly that the solvent is assuming a special role (presumably nucleophilic participation) in this medium.

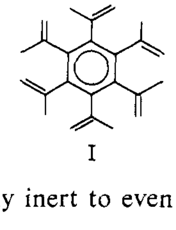
[13] W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940).

Edward M. Arnett, Wesley G. Bentrude, Peter McC. Duggleby
Department of Chemistry, University of Pittsburgh
and Mellon Institute, Pittsburgh, Pennsylvania 15213
Received February, 4, 1965

Hexaisopropenylbenzene, an Unreactive Polyolefin[1,2]

Sir:

Formally, hexaisopropenylbenzene (I) is a polyvinylbenzene and might at first glance be expected to exhibit high reactivity in addition and polymerization reactions.



I

Actually, it is nearly inert to even potent double-bond reagents.

In classical terms, this might suggest some unusual kind of "aromaticity." However, this interpretation is theoretically unattractive and is not supported by n.m.r., infrared, or ultraviolet spectra. The surprising lack of reactivity is, however, quite consistent with the mutual shielding of adjacent isopropenyl groups since the transition state for addition would require creation of a system even more tightly congested than that of hexaisopropylbenzene, which we have described recently.[3]

Preparation. Diisopropenylacetylene[4] (0.16 mole) and dicobalt octacarbonyl[3] (0.053 mole) were heated at reflux in 125 ml. of Skellysolve C. Solvent was removed from the black solution and the viscous product was filtered. Extraction of the residue with Skellysolve B yielded finally a 4% yield of I melting at 260–263° after three recrystallizations from this solvent. The structure was assigned on the basis of the following data: (1) method of synthesis; (2) analysis (*Anal.* Calcd. for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.74; H, 9.29); (3) molecular weight (the theoretical value of 318 was found by mass spectrometry and 294 by vapor pressure osmometer); (4) appearance of the n.m.r. spectrum (nearly identical with that of α-methylstyrene, except for slight shifts and the complete absence of aromatic protons; in CS_2, multiplets integrating in the ratio 1:1:3 were found at τ 4.96, 5.35, and 8.07 p.p.m. (α-methylstyrene: τ 4.73, 5.00, and 7.90 p.p.m.)); (5) infrared spectrum[5] (in CS_2 also like that of methyl styrene with sharp bands at 3050, 2980, 2940, 1790 (overtone), 1635, 1360, 1220, and 885 cm.$^{-1}$ (strongest in spectrum)); (6) ultraviolet spectrum (essentially that of an unconjugated polyolefin, indicating that the blocked vinyl groups are twisted out of the plane of the benzene ring). Strong absorption in the far-ultraviolet gradually dropped to a negligible value at about 310 mμ. At 290 mμ, a small shoulder (ϵ 284) may be compared with one (ϵ 100) for α-methylstyrene at the same wave length. A gentle shoulder at 225 mμ (ϵ 2.55 $\times$ 10^4) may be compared with a peak at 243 mμ (ϵ 1.02 $\times$ 10^4) for α-methylstyrene).

Attempted Reactions. Compound I resisted attempts to hydrogenate it at room temperature in cyclohexane in the presence of 5% palladium, rhodium, or platinum on carbon. It was recovered unchanged from standard hydroboration treatment[6] with sodium borohydride in diglyme followed by boron trifluoride etherate and aqueous acetic acid work-up.

Compound I was at first inert to 5% bromine in carbon tetrachloride, but on standing some substitution occurred as shown by HBr evolution. Treatment of I with 2% potassium permanganate in acetone for 40 hr. at room temperature produced no color change relative to an acetone control. There was no visible evidence of interaction with tetracyanoethylene or of compound formation with silver nitrate in ethanol.

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[1] Crowded Benzenes. V. See *Tetrahedron Letters*, No. **50**, 3803 (1964), for previous paper in this series.

[2] Supported by National Science Foundation Grant G-14583.

[3] E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

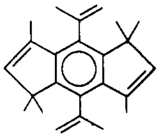
[4] D. T. Mitchell and C. S. Marvel, *ibid.*, **55**, 4277 (1933).

[5] A large band was found in the far-infrared at 525 cm.$^{-1}$. This is far outside the range for hexasubstituted benzenes given by Jakobsen, which we used for structure proof in our previous paper.[3] Closer scrutiny indicates that Jakobsen's assignment was based on a single compound, and since we have found several hexasubstituted benzenes which give no band at all in this region, we consider his correlation to be of little value for this series.

[6] H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

Treatment of I in purified isooctane with ozone from a Welsbach T-23 ozonizer resulted in "breakthrough" of ozone into a 2% potassium iodide trap after approximately the same interval (4 min.) as was required for a solvent blank. Normal olefins are completely ozonized before breakthrough occurs. Further treatment for 1.5 hr. gave about the same 3.2-fold excess of ozone used by Haaijman and Wibaut[7] for ozonolysis of *o*-xylene. This was apparently sufficient to produce extensive attack since nearly twice the amount needed to ozonize the six double bonds was absorbed.

Although relatively impervious to addition of large external reagents to its system of double bonds, I is sensitive to photolysis and attack by strong acid. The photolysis product is currently under examination. Sulfuric acid (96%) apparently converts I to an orange carbonium ion whose color is half quenched between 65 and 70% H_2SO_4[8] and which, upon complete quenching with aqueous base, yields an isomer for which we tentatively advance structure II on the basis of n.m.r., infrared, and mass spectra.[8a]



II

[7] P. W. Haaijman and J. P. Wibaut, *Rec. trav. chem.*, **60**, 842 (1941).

[8] N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).

[8a] Note Added in Proof. The above interpretation of the low reactivity of hexaisopropenylbenzene is supported by the fact that we have just prepared hexavinylbenzene and find it to exhibit normal reactivity to double bond reagents.

[9] National Institute of Health Predoctoral Fellow.

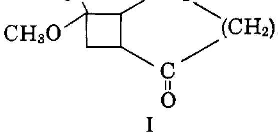
Edward M. Arnett, J. Martin Bollinger, Joseph C. Sanda[9]
Department of Chemistry, University of Pittsburgh
and Mellon Institute, Pittsburgh, Pennsylvania 15213

Received March 11, 1965

trans-2-Cycloheptenone

Sir:

In a previous study of the photochemical addition of conjugated enones to other unsaturated substances it was found that 1,1-dimethoxyethylene is especially effective in capturing the reactive species which arise from the n-π^* electronic transition of 2-cyclopentenone and 2-cyclohexenone.[1] The products resulting from these ketones and 1,1-dimethoxyethylene are I, $n = 1$, and I, $n = 2$ (as a mixture of *trans*- and *cis*-fused isomers in a ratio of 2.3:1), respectively. The reaction of *cis*-2-cyclooctenone was found to involve prior photoisomerization[2] to *trans*-2-cyclooctenone followed by a nonphotochemical cycloaddition to form the adduct II.



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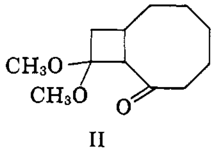
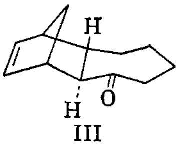


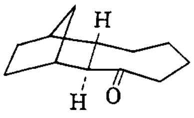
II

Under the same conditions the irradiation of a mixture of 1,1-dimethoxyethylene (15-fold excess) and 2-cycloheptenone gave no 1:1 adduct, but only self-condensation products (mainly dimers) of the ketone. The rate of self-condensation of 2-cycloheptenone was close to the rate of *cis* → *trans* isomerization of 2-cyclooctenone under the same photochemical conditions. This and other considerations, including the recent detection of *trans*-cycloheptene in these laboratories,[3] suggested that the rapid photodimerization of *cis*-2-cycloheptenone might be the result of the intervention of the highly strained *trans* isomer, and an investigation of this possibility was undertaken. Starting with the assumption that *trans*-2-cycloheptenone preferentially reacts with itself rather than with 1,1-dimethoxyethylene or *cis*-2-cycloheptenone, the most promising approach to its interception appeared to be the use of a reactive 1,3-diene which could make available a low-energy Diels–Alder pathway.

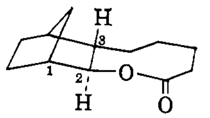
Irradiation ($\lambda > 300$ mμ) of a mixture of *cis*-2-cycloheptenone and cyclopentadiene (excess) at *ca.* $-50°$ afforded a single 1:1 adduct ($C_{12}H_{16}O$) in 95% yield, which is formulated as III on the basis of chemical and physical data.[4,5] The adduct was homogeneous as judged by vapor phase chromatographic (v.p.c.) and thin layer chromatographic (t.l.c.) analysis. The presence of a ketonic carbonyl group was indicated by infrared absorption at 5.86 μ; n.m.r. analysis revealed two olefinic protons as quartets centered at 5.93 and 6.20 p.p.m.[6] (the peaks of the latter somewhat broadened) with the splittings for each proton ~5.3 and ~2.6 c.p.s.; peaks due to 14 other protons appeared upfield. Mass spectrometry indicated a parent peak of *m/e* 176. Catalytic hydrogenation over palladium afforded a saturated ketone (IV) by addition of two hydrogens to the olefinic bond. Treatment of the dihydro derivative IV with peracetic acid produced the crystalline saturated lactone V,[4] which shows lactonic carbonyl absorption at 5.78 μ. Significantly, the lactone exhibits a single n.m.r. peak due to the proton of >CH—O—C(=O)- at 3.92 p.p.m. with a band width at half-height of 4.5 c.p.s. The width of this peak indicates that the proton at C-2 must be *trans* to that at C-3, and further that the proton at C-2 must be *endo*.[7]



III



IV



V

Saponification of V afforded a crystalline hydroxy acid, m.p. 109–111°, which was oxidized by chromic

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[1] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

[2] P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

[3] E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

[4] Satisfactory elemental analyses were obtained.

[5] *cis*-2-Cycloheptenone was prepared by chromic acid oxidation of 2-cycloheptenol [A. C. Cope, T. A. Liss, and G. W. Wood, *ibid.*, **79**, 6287 (1957)].

[6] All chemical shifts are expressed as p.p.m. downfield from internal tetramethylsilane.

[7] The following are the expected values of vicinal coupling constants for the norbornane system $J_{2,3}$ (*exo,exo*) ~ 10 c.p.s., $J_{2,3}$ (*endo,endo*) ~ 7 c.p.s., $J_{2,3}$ (*exo,endo*) ~ 4 c.p.s., $J_{1,2}$ (bridgehead *endo*) ~ 0 c.p.s., $J_{1,2}$ (bridgehead *exo*) ~ 3.5 c.p.s. See, for example, P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); also E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964). From these values it is apparent that only stereoformula V satisfies the n.m.r. data for the lactone.