

Compounds VII and VIII are the products expected from the 2,2,2-triphenylethyl radical, which rearranges with great ease,⁹ while IX probably results from a rapid secondary cage recombination involving the unrearranged species and the *t*-butoxy radical. The probable precursor of IV and V is the radical formed by addition of a methyl radical (from β -scission of the *t*-butoxy fragment) to III. The origin of X is not clear; an interesting possibility is that it results from induced decomposition of Ia by one or more radicals capable of donating hydrogen.¹⁰

Reaction mixtures from the decomposition of Ib and Ic in chlorobenzene at 100° were saponified and then acidified to give mixtures of phenols which were examined by gas chromatography. Perester Ib yielded only phenol and *p*-methoxyphenol, while Ic gave exclusively phenol and *p*-nitrophenol; thus the transition state for the aryl migration is of the Ar₁-5 type rather than Ar₂-6.¹¹ From quantitative analyses of the phenolic products, the relative migratory aptitudes of phenyl (corrected by a statistical factor of two), *p*-methoxyphenyl, and *p*-nitrophenyl were determined to be 1.0:4.0:0.25.¹² A Hammett plot of these data using σ^+ constants gives an excellent correlation with ρ equal to -0.78. Although the general applicability of this correlation remains to be demonstrated, the electrophilic nature of the postulated acyloxy radical intermediate is clearly implied by the results already in hand.¹³

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(9) (a) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); (b) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

(10) W. R. Foster and G. H. Williams, *J. Chem. Soc.*, 2862 (1962) have cited evidence for the formation of benzoic acid in the induced decomposition of benzoyl peroxide by phenylcyclohexadienyl radicals.

(11) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

(12) These numbers do not necessarily represent *intrinsic* migratory aptitudes, since there is no guarantee that the phenyl reference group migrates at the same rate in both cases.

(13) A study of the thermal decomposition of 3,3,3-triphenylpropanoyl peroxide has recently been carried out by H. M. Weiss, Ph. D. thesis, Rutgers University, 1962. The mechanism proposed is quite different from that suggested here for decomposition of the related *t*-butyl peresters.

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A New Noncyclic Butadiene Oligomer: *trans*-3-Methylhepta-1,4,6-triene

Sir:

Wilke has opened a new field of cyclic diene oligomers such as cyclodecatriene.¹

In the course of study on the mechanism of stereospecific high polymerization of butadiene, we have found that cobalt-containing catalysts can yield a new noncyclic butadiene oligomer in high yield.

Oligomerization of butadiene was effected in the absence or presence of an inert solvent at slightly above room temperature using dicobalt octacarbonyl-triethylaluminum catalyst. A new triene (I) of b.p. 117° (760 mm.), n_D^{20} 1.4657, d_4^{20} 0.7570, was obtained in 90% yield.

(1) G. Wilke, *Angew. Chem.*, **69**, 397 (1957); *ibid.*, **71**, 574 (1959); G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); G. Wilke, *Angew. Chem.*, **72**, 581 (1960); G. Wilke, *ibid.*, **73**, 33, 755, 756 (1961).

Anal. Calcd. for C₈H₁₂: C, 88.82; H, 11.18. Found: C, 89.20; H, 11.20.

A typical procedure is as follows. All operation was carried out under pure nitrogen. In a stainless-steel autoclave of 12-l. capacity were placed 13.6 g. (80 mmoles) of crystalline dicobalt octacarbonyl and 4300 g. (80 moles) of dried "pure grade" butadiene. After the autoclave was chilled to 0°, 272 g. (2.4 moles) of triethylaluminum was added slowly under gentle stirring. The temperature was raised gradually to 40° and kept for 48 hr. with stirring. The reaction mixture was again chilled to 0° and the organometallic catalysts were destroyed by *tert*-butyl alcohol.

Gas chromatographic analysis of an aliquot from the reaction mixture indicated that 60% of butadiene was converted to dimers of which 90, 8, and 1% were I, 4-vinylcyclohexene-1 plus a *n*-octatriene, and 1,5-cyclooctadiene, respectively. Fractional distillation gave I as a main fraction, b.p. 69–73° (180 mm.).

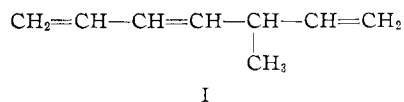
Pure substance for analytical purpose was obtained by preparative gas chromatography. From the molecular weight found by the cryoscopic method in benzene and quantitative hydrogen absorption with platinum catalyst, the product was found to be a dimer which contains three double bonds. The infrared spectrum of the hydrogenated product was identical with that of 3-methylheptane. The ultraviolet absorption spectrum (λ_{\max} 227 m μ (log ϵ 4.40)) indicated conjugation of two double bonds but not of three. The infrared spectrum (900 (s), 910 (s), 948 (m), 1000 (m), 1368 (m), 1410 (m), 1450 (s), 1603 (s), 1636 (s), 1800 (m); s, strong, m, medium) showed the presence of C—CH₃, =CH₂, and conjugated double bonds. Nuclear magnetic resonance data showed the presence of one CH₃—CH (doublet τ = 8.9, J = 7.0) and two —CH₂— and four =CH— groups.

A maleic anhydride addition reaction gave further information. Thus, the infrared spectrum of the adduct (m.p. 61–62°) showed one terminal vinyl group was still retained.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 69.82; H, 6.90.

Moreover, the ease of the Diels–Alder reaction suggests that the inner —CH=CH— group probably has *trans* configuration, as shown in the *cis*- and *trans*-piperylene² and 1,3,5-hexatriene isomers.³

The structure of the triene is thus best formulated as 3-methylhepta-1,4,6-triene (I).



The absence of the geometrical and/or structural isomers, such as normal octatriene, in I was confirmed from the quantitative yield of the Diels–Alder reaction and from the gas chromatographic analysis.

The infrared absorption spectrum of the reaction between the cobalt carbonyl and triethylaluminum indicated complete disappearance of the CO stretching bands (terminal CO: 2028 (s), 2037 (m), 2050 (s), 2065 (m), 2077 (s), bridge CO: 1853 (s), 1862 (m)), irrespective of the presence or absence of butadiene monomer. The best catalytic activity, however, was obtained when the two components were admixed in the presence of the monomer, resulting in a homogeneous solution.

(2) E. H. Farmer and F. L. Marren, *J. Chem. Soc.*, 3221 (1931); R. F. Robey, C. E. Morrell, and H. K. Wiese, *J. Am. Chem. Soc.*, **63**, 627 (1941); J. A. Norton, *Chem. Rev.*, **31**, 349 (1942); D. Craig, *J. Am. Chem. Soc.*, **66**, 1006 (1943).

(3) J. C. H. Hwa, P. L. De Benneville, and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

Without monomer metallic cobalt was soon precipitated at room temperature.

Thus, the stereospecificity of the catalyst can be ascribed to the "naked" Co(O) (d^9) which may loosely be coordinated by butadiene and/or $AlEt_3$ molecules and not to the metallic cobalt (ground state, $3d^7 4s^2$).

If the same catalyst system is applied in a solvent containing highly electronegative groups, *e.g.*, CH_2Cl_2 , it produces solid polybutadiene of high 1,4-*cis* content. This may be explained by the strong ligand field effects of chlorine on the electronic structure of Co(O).

It is to be noted that Ni(O) has a filled 3d orbital of spherical symmetry and, in contrast to Co(O), it catalyzes the formation of the cyclic trimer of butadiene.¹ Again, this reaction should be carried out in a hydrocarbon medium of weak ligand field.

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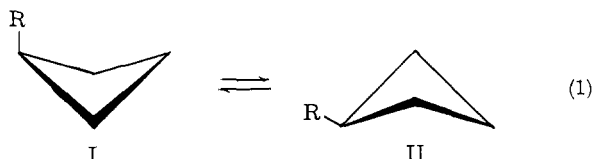
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Conformational Studies of Cyclobutane Systems¹

Sir:

Isolated attempts have been made to detect the presence of nonplanarity in cyclobutane rings. Significant deviations from planarity have been measured for cyclobutane,^{2,3} octafluorocyclobutane,⁴ octachlorocyclobutane,⁵ and bromocyclobutane.⁶ The results in the first two cases, however, have not been without controversy. It was the object of the present work to devise a fairly general, but still straightforward, method of detecting the presence and determining the magnitude of puckering in substituted cyclobutane rings, and to ascertain whether the results could be interpreted in terms of an equilibrium between axial (I) and equatorial (II) conformations.



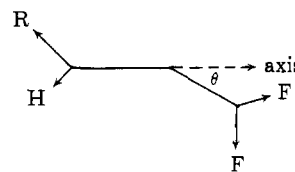
Puckering of the ring reduces 1,2 substituent interactions by staggering adjacent groups, with relatively small changes in the bond angles. Monosubstituted cyclobutanes, like monosubstituted cyclohexanes, are expected to show a preference for the equatorial conformation II, which should reduce 1,3 interactions.

Dipole-moment measurements have particular value for the determination of the average degree of puckering of variously substituted 1,1-difluorocyclobutanes. The

	R	R'	R''
IIIa	$p\text{-NO}_2\text{-C}_6\text{H}_4$	H	H
IIIb	C_6H_5	H	H
IIIc	C_6H_5	H	Cl
IIId	Cl	H	Cl
IIIe	C_6H_5	Br	H

geometries of 1,1-difluoro-3-(*p*-nitro)-phenylcyclobutane (IIIa) and of 1,1-difluoro-3-phenylcyclobutane (IIIb) were ascertained in this manner, with the aid of the

assumption that the angle of puckering, θ , is the same for both compounds.



The dipole moments of IIIa and of IIIb were found to be (benzene solution at 27.5°), respectively, 2.81 and 2.09 ± 0.02 D. The C-H bond moment was taken to be 0.4 D., with hydrogen negative with respect to carbon.⁷ This choice is not vital, because the moments of the methine hydrogens and of the methylene hydrogens tend to cancel each other. With this convention, the group moment for C-(*p*-nitro)phenyl was calculated to be 4.85 D. from the dipole moment of *p*-nitrotoluene, 4.45 D. Consideration of the vector quantities which are involved yields four equations in four unknowns: θ , the angle of puckering; the CF_2 bond moment; and $\phi(\text{IIIa})$ and $\phi(\text{IIIb})$, the angles which the molecular moments make with the indicated axis. The unique solutions were found to be $\theta = 26^\circ 45' \pm 40'$; $\phi(\text{IIIa}) = 76^\circ 30' \pm 40'$ (above the minus direction of the axis); $\phi(\text{IIIb}) = 26^\circ 40' \pm 40'$ (below the plus direction of the axis); $CF_2 = 2.54 \pm 0.01$ D. The puckering angle obtained in this manner compares favorably with the results in other systems: octafluorocyclobutane, 20° ⁴; octachlorocyclobutane, 22° ⁵; and bromocyclobutane, 29° .⁶ Although the experimental error in the measured values of the dipole moments is small, the calculated value of θ is subject to the usual limitations for determination of molecular geometry from dipole moments.⁷ It is important to recognize also that θ is an *average* angle of puckering, calculated assuming the geometry of the dominant species, II. The value of θ might be refined by resolution of the molecular moment into components for each conformation. This will require more precise knowledge of the geometry of the axial conformation (*vide infra*). However, when the equilibrium is far on the side of one isomer, the correction has been shown to be small.

The possibility of extending this result to other systems was investigated by nuclear magnetic resonance spectroscopy (n.m.r.). For nonplanar compounds such as IIIb, the chemical-shift difference, δ , between the nonequivalent fluorine atoms will vary with temperature as the equilibrium, $I \rightleftharpoons II$, shifts.⁸ Lower temperatures should favor conformer II, whereas higher temperatures will bring about an approach to equal population of both conformations. Absence of a temperature effect, conversely, should indicate planarity. The fluorine magnetic resonance spectra of six compounds, IIIb-e, IV, and V,¹⁰ accordingly were investigated at five temperatures ranging from -85 to $+140^\circ$. The chemical shifts (Table I) were measured to ± 1 c.p.s. by the side-band technique; coupling of the fluorine nuclei with the protons was removed by simultaneous irradiation of the sample at the proton frequency. The cyclobutene IV and the cyclobutanone

(7) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 200 ff.

(8) Although the data are interpreted in terms of a classical equilibrium between I and II, they could also be accommodated by consideration of an asymmetric potential well which lacks the two distinct minima required by the two conformations. However, distinct minima have been demonstrated spectroscopically for cyclobutane² and trimethylene oxide.⁹

(9) S. I. Chan, J. Zinn, and W. D. Gwinn, *J. Chem. Phys.*, **34**, 1319 (1961).

(10) We are indebted to Dr. D. C. England for furnishing us with this sample.

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(3) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(4) H. P. Lemaire and R. L. Livingston, *ibid.*, **74**, 5732 (1952).

(5) T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

(6) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).