fluoroborate. The reaction mixture was stirred for 30 min and then refluxed briefly (10 min). Water (100 ml) was added and the aqueous layer was washed with two 25-ml portions of pentane. The combined pentane extracts were washed with water (2 × 20 ml) and dried ($MgSO_4$), and the solvent was removed on a rotary evaporator without external heating to give 2.11 g (71%) of a light red liquid. Gc analysis (98°; 67 ml/min) of this material showed three components which were collected and shown to be (in order of elution) **3** (30%), **4** (46%), and **2** (24%), as described in the text. A glc sample of **2** gave a satisfactory analysis. *Anal.* Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.97; H, 10.94. The ir spectra on the neat liquids showed: **2**, 3040, 2980 (s), 2940, 2900, 1480, 1390, 1360, 790, 770, 710 (s), 690 (s); **3**, 3055, 3045, 2995 (s), 2900, 1470 (s), 1395, 1385, 1365, 790 (s), 755 (s), 715 (s); **4**, 3050, 2980 (s), 2900, 1460 (s), 1390, 1360, 745 (s), 725 (s), 695 (s) cm^{-1}.

***tert*-Butyltropylium Fluoroborate.** This ion could not be prepared directly from 7-*tert*-butylcycloheptatriene by hydride exchange with triphenylmethyl fluoroborate. However if 7-*tert*-butylcyclohepatriene is heated at 170° for 4.5 hr, the resulting mixture of isomers, containing only 14% of the 7 isomer, does undergo hydride exchange.[44] Thus to 4.0 g (0.012 mol) of triphenylmethyl fluoroborate, in 20 ml of methylene chloride, was added 2.42 g (0.0163 mol) of the *tert*-butylcycloheptatriene isomer mixture. The solution was allowed to stand for 3.5 hr. The solvent was then evaporated and the solid residue was washed thoroughly with ether. Three recrystallizations from ethanol gave 2.55 g (90%) of white solid, mp 146.5–148.4. This material was used directly in the reaction below.

Reaction of *tert*-Butyltropylium Tetrafluoroborate with Methyllithium. To 4.8 ml of a 1.67 *M* ether solution of methyllithium (0.176 g, 8.01 mmol) further diluted with 20 ml of ether was added 1.50 g (6.42 mmol) of *tert*-butyltropylium fluoroborate. The reaction mixture was stirred for 15 min, and 100 ml of water was added. The ether layer was separated, dried ($MgSO_4$), and concentrated to give 0.87 g (84%) of crude product. This material was distilled to give 0.40 g of colorless liquid, bp 64° at 6.7 mm. Gc analysis (90°, 60 ml/min) showed three components which were collected and shown to be (in order of elution) the 2- (40%), 3- (42%), and 1- (18%) *tert*-butyl-7-methylcycloheptatriene isomers as described in the text. The ir spectrum of **6** showed: 3060, 3000 (s), 2910, 1525, 1460, 1390, 1370, 1260, 760, 705 (s) cm^{-1}.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work under Grant No. NSF GP-24392.

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[44] This technique of using isomerized cycloheptatriene isomers to prepare substituted tropylium ion, discovered independently in this laboratory, has been used to prepare phenyltropylium fluoroborate[45] although this salt can be prepared directly from 7-phenylcycloheptatriene.

[45] K. Shen, W. E. McEwen, and A. P. Wolf, *Tetrahedron Lett.*, 827 (1969).

Valence Bond Isomers of Aromatic Systems. Bicyclo[2.2.0]hexa-2,5-dienes (Dewar Benzenes)[1]

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Received September 30, 1970

Abstract: The first synthesis and identification of the benzene valence bond isomers, Dewar benzenes, are described in detail. In one case 1,2,4-tri-*tert*-butylbenzene is converted by ultraviolet irradiation into 1,2,5-tri-*tert*-butylbicyclo[2.2.0]hexa-2,5-diene (**28**). In the second, parent bicyclo[2.2.0]hexa-2,5-diene (**4**) was obtained by oxidative decarboxylation of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic acid, the anhydride of which is prepared by photolysis of 1,2-dihydrophthalic acid anhydride. Related chemistry is described, including: proof of structure of Dewar benzenes **4** and **28**; the ultraviolet-induced conversion of *o*-di-*tert*-butylbenzene to *m*-di-*tert*-butylbenzene and interconversion of *m*- and *p*-di-*tert*-butylbenzenes; photolysis of [2.2]paracyclophane and certain substituted 1,2-dihydrophthalic anhydrides. Theoretical aspects of the photochemical formation and properties of Dewar benzenes are discussed.

Firmly based within the broad and intricate framework of organic chemistry, the benzene ring has served as a stable platform upon which have been performed during the last century a great variety of interesting and important chemical exercises. Until recent years, no serious question about the prevailing integrity of this structural unit had been raised, although it is of historical interest that, as concepts, certain valence bond isomer representations had appeared in the earlier literature. For reasons stated below, we started during the early 1960's to give consideration to the prospect of preparing and isolating bicyclo[2.2.0]hexadienes (Dewar benzenes), and in the ensuing few years, two examples of such benzene valence bond isomers resulted from our laboratory efforts.[1] In related programs, there were synthesized or detected valence bond isomers of other aromatic systems: *cis*- and *trans*-9,10-dihydronaphthalenes,[3,4] Dewar tropylium ion,[5] and Δ^2-cyclopropenyl ketones[6], the aromatic counterparts being 1,3,5,7,9-cyclodecapentaene, tropylium ion, and substituted furans, respectively. In addition to biscyclopropenyls,[7]

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[1] The synthesis of bicyclo[2.2.0]hexadienes was first announced in two Communications to the Editor (E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); **85**, 3297 (1963)) and was presented as part of a lecture, "Valence Bond Isomers of Aromatic Systems," by E. E. van Tamelen: Abstracts, American Chemical Society 18th National Organic Symposium, Columbus, Ohio, June 1963.

[2] Address correspondence to this author at: Department of Chemistry, Stanford University, Stanford, Calif. 94305.

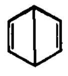
[3] E. E. van Tamalene and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963).

[4] E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).

[5] E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *ibid.*, **90**, 1372 (1968).

[6] E. E. van Tamelen and T. H. Whitesides, *ibid.*, **90**, 3894 (1968).

[7] Bistriphenylcyclopropenyl, the first formal benzene valence bond isomer to have been observed, was prepared by R. Breslow and P. Gal, *ibid.*, **81**, 4747 (1959). Since the appearance of this and our original work, a variety of other benzene valence bond isomers have been reported. No specific attempt will be made in this paper to refer to these cases, although a partial list appears in ref 11.



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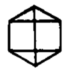

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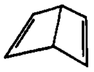
three benzene valence bond isomers are apparent: the bicyclohexadiene **1** (Dewar benzene);[8] the tricyclohexene **2** (benzvalene);[9] and the tetracyclohexane **3** (prismane).[10] Originally conceived as *planar*, alternative (electronic) expressions for the structure of benzene, these designations gain independent physical reality as nonplanar constructions **4**, **5**, and **6**, which



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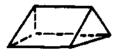
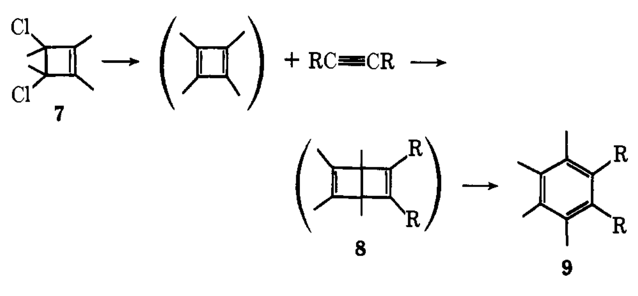
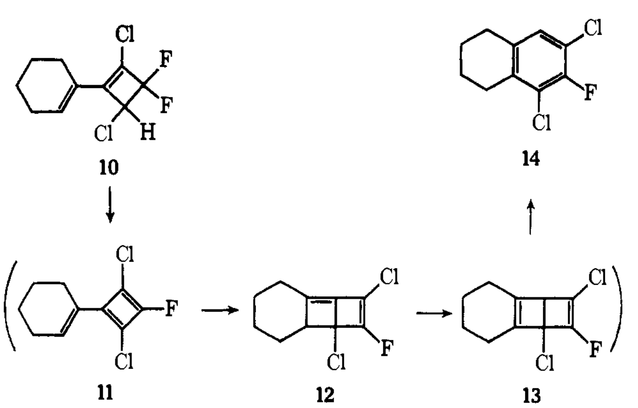


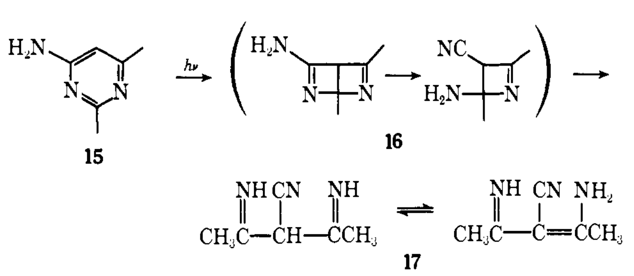
6

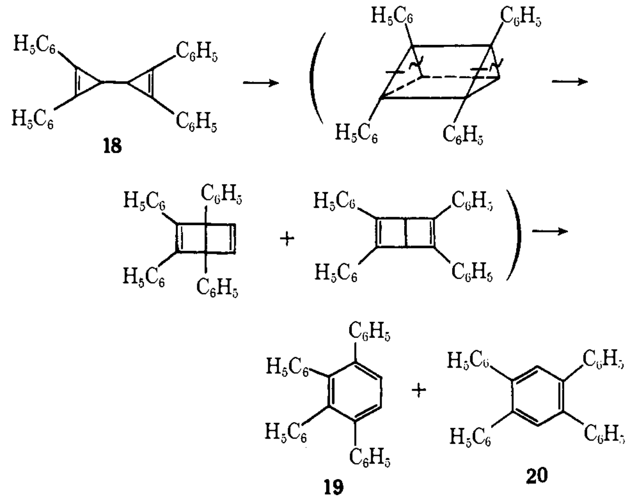
belong, respectively, to the κ^1, κ^2, and κ^3 series of valence bond isomers.[11] Of the three, the Dewar benzene system represents, in respect to geometrical distortion and electronic modification, the most subtle modification of the planar system; it thus might be expected to be the entity most easily convertible to the aromatic counterpart, and therefore the most transient of the trio in this sense. Because of these reasons, we originally regarded the obtention of a nonplanar Dewar benzene as the most challenging synthetic goal, and accordingly took up studies along such lines.

Recorded by Sir James Dewar as a less desirable alternative to the Kekulé proposal for benzene,[8] the planar bicyclo[2.2.0]hexadiene structure has retained importance as a minor contributor to the overall electronic structure of benzene in the valence bond method.[12] During the last decade, Dewar benzene structures have been occasionally invoked as presumed, unisolated intermediates in certain unusual transformations. For example, 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**7**), on treatment with metallic zinc in the presence of 2-butyne or diethyl acetylenedicarboxylate, affords the benzene derivative **9** supposedly *via* the unstable nonplanar Dewar benzene **8**.[13] Similarly, triethylamine-induced elimination of hydrogen fluoride from the cyclohexenylcyclobutene **10** leads to formation of the tetralin derivative **14**, for which reaction the intermediates **11–13** were proposed.[14] In the heterocyclic series, the novel formation of 2-amino-3-cyanopent-2-en-4-imine (**17**) from 2,6-dimethyl-4-aminopyrimidine (**15**) may be initiated by photoinduced formation of a Dewar pyrimidine (**16**).[15] Finally, it has been suggested that the isomerization of the tetraphenylbicyclopropenyl **18** to the tetraphenylbenzenes **19** and **20** involves transient Dewar benzene intermediates, in addition to prismanes.[16] In all of these cases, the idea of a Dewar structure is interpretative or conjectural—neither was the Dewar-type molecule isolated, nor was additional evidence adduced for its intermediacy.









There were several reasons for hoping that a Dewar benzene would possess stability sufficient to permit isolation or, at least, detention. It was known[17,18] that cis and trans 3,4-disubstituted cyclobutenes **21** and **22**

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[8] (a) J. Dewar, *Proc. Roy. Soc. Edinburgh*, 84 (1866–1867); (b) C. K. Ingold, *J. Chem. Soc.*, **121**, 1133 (1922). (c) W. Baker, *Chem. Brit.*, **1**, 191 (1965).

[9] E. Hückel, *Z. Elektrochem.*, **45**, 752, 760 (1937).

[10] A. Ladenburg, *Ber.*, **2**, 140 (1869); **5**, 322 (1872).

[11] E. E. van Tamelen, *Angew. Chem.*, 77, 759 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).

[12] (a) E. Hückel, *Z. Phys.*, **70**, 204 (1931); (b) G. W. Wheland, "Advanced Organic Chemistry," Wiley, New York, N. Y., 1960, pp 117–118.

[13] C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961).

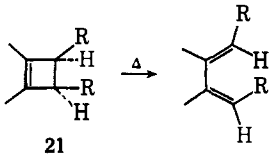
[14] C. M. Sharts and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 871 (1961).

[15] K. L. Wierzchowski, D. Shugar, and A. Katritsky, *ibid.*, **85**, 827 (1963).

[16] R. Breslow in "Molecular Rearrangements. Part I," P. de Mayo, Ed., Interscience, New York-London, 1963, pp 243–245, R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965).

[17] E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 14 (1958).

[18] R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959).



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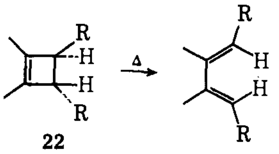
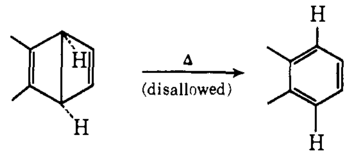
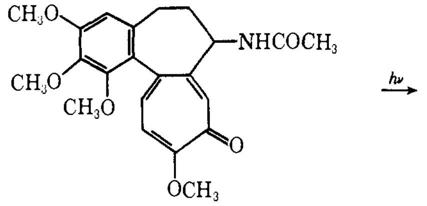


22

undergo highly stereospecific, thermal ring opening, each type giving rise to only a single diene geometrical isomer. Applying these results to the case at hand, one recognizes that isomerization of a (cis-fused) Dewar benzene to the aromatic counterpart could *not* proceed by the stereochemically preferred ring-opening pathway,



and thus a barrier of significant magnitude would confront the nonaromatic partner. It was also known that colchicine (**23**) is convertible to an irradiation product,



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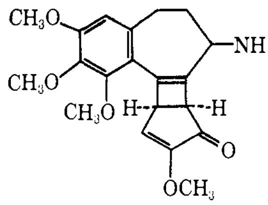

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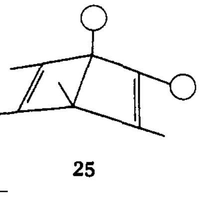
lumicolchicine (**24**), in which the nonbenzenoid aromatic ring has been transformed into the isomeric [3.2.0]bicycloheptenone system,[19] an overall change which finds subsequent parallel in simpler systems.[20] In this example, we find present in the product a valence bond isomer which is distinctly unstable relative to the aromatic progenitor, although probably not to the degree as in the benzene–Dewar benzene case. Despite the above encouraging hints, no reliable estimate as to the *degree* of stability of Dewar benzene was justified, and on this account two experimental programs were initiated concurrently, one designed to generate one of the most stable representatives imaginable, and a second planned to provide the simple parent case, unsubstituted Dewar benzene **4**.

In a given benzene–Dewar benzene pair, bulky substituents at positions 1 and 2 should alter the energy relationship of the two structures so as to help stabilize, by virtue of steric factors, the nonaromatic member. As can be appreciated from the stylized formulas **25** and **26**, steric interference between two large ortho groups can be severe in the aromatic case, whereas in the (nonplanar) Dewar structure, the 1 substituent is affixed perpendicular to the approximate plane of the ring, while the 2 substituent lies roughly in that plane, well out-of-touch with the neighboring group. Clearly, such steric factors will help prevent isomerization of the type **25** Dewar benzene to the aromatic system. In addition, large, unreactive substituents on the ring will tend to fend off attacking agents and thus protect the bicyclohexadiene nucleus, once formed, from degradation, polymerization, or other disruptive phenomena.



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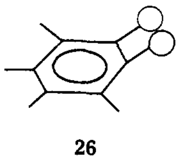

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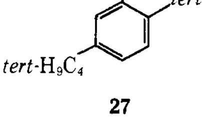
In view of the above considerations, attempts were made to induce, by irradiation means, the conversion of a *o*-di-*tert*-butylbenzene to a 1,2-di-*tert*-butylbicyclohexadiene. 1,2,4-Tri-*tert*-butylbenzene (**27**)[21] was selected for initial attempts. Irradiation with a Hanovia type L ultraviolet lamp (Vycor filter) of this aromatic in ether solution resulted in enhanced absorption in the 265–270-mμ region and diminution of the extinction at lower wavelengths, changes which ceased after 2 hr of illumination. After such treatment, there were isolated hydrocarbon materials which appeared as two spots by tlc (silica gel-cyclohexane); under the above conditions, only traces of other products were formed. Preparative tlc provided the faster moving component ($R_f = \sim 0.7$) as a colorless oil, and the slower moving fraction ($R_f = \sim 0.5$) as a bright yellow liquid. The latter material exhibited an ultraviolet spectrum very similar to that of the crude irradiation mixture (λ_{max}^{ether} 260 mμ). On the basis of uv, visible, and nmr spectra, this fraction appeared to be a mixture of (1) the original aromatic, (2) fulvenoid product.[22] and (3) 1,3,5-tri-*tert*-butylbenzene, formed by isomerization of starting material.[23]

The second product was found to be a stable hydrocarbon, solid below 0° and isomeric with 1,2,4-tri-*tert*-butylbenzene. Purification of the tlc product was accomplished by distillation at room temperature (10^{-7} mm pressure). The volatility and chromatographic behavior of the irradiation product suggested that it was monomeric, and this surmise was confirmed by mass spectrometric determination (parent peak 246)[24] and by its osmometric molecular weight (274 in benzene solution at 39°).[25] On being heated to 200° for 15 min, the photohydrocarbon was converted in good yield to 1,2,4-tri-*tert*-butylbenzene, as evidenced by thin-layer chromatographic, infrared spectral, and mixture melting point comparison. In accordance with the favored structure **28**, only end absorption (λ^{ether} 220 mμ, ϵ



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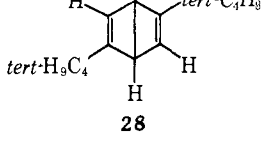

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[19] E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).

[20] O. L. Chapman and D. J. Pasto, *J. Amer. Chem. Soc.*, **80**, 6685 (1958); **82**, 3642 (1960).

[21] C. Hoogzand and W. Hubel, *Tetrahedron Lett.*, 637 (1961).

[22] Fulvene is an irradiation product of benzene itself: H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

[23] In this connection, see K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 87, 4006 (1965).

[24] Kindly provided by Professor C. Djerassi, Stanford University.

[25] Kindly provided by R. W. Rinehart, The Upjohn Company.

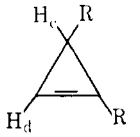
1800) appeared in the usual ultraviolet region (>215 mμ). Carbon–carbon double bond stretching peaks appear in the high-wavelength infrared region (6.26 and 6.46 μ) characteristic of cyclobutene systems.[26]

The proton magnetic resonance spectrum of the new hydrocarbon (Table I) provided further important clues as to its structural nature. In addition to a peak for a single proton appearing in the methine region (τ 6.80), signals ascribable to olefinic hydrogens appear at τ 3.87 and 3.95; further, the higher field olefinic proton and the methine hydrogen split each other, whereas the lower field olefinic proton is unsplit. It is evident that there must be *two* trisubstituted double bonds in the molecule, implying that the ring system is bicyclic.[27] Assuming nonconjugation of the double bonds and without considering chemical plausibility, a number of structures loosely accommodating the above data can be entertained. Of these, save for the [2.2.0]bicyclohexa-2,5-diene system, all feature one or two three-membered rings, and except for two cases (alkylidenecyclopropanes **29b** and **29c**), all are cyclopropene type **29a**. Other investigations[28] have measured the chemical shifts of various hydrogens on the latter ring system, with the finding that a proton (H_c) on the saturated ring carbon appears at τ 8.6–8.7, while a hydrogen (H_d) on the double bond falls at τ 3.0–3.45. The proton resonances of the photohydrocarbon lie distinctly outside these ranges, and beyond that, are reasonable for the proposed structure (cyclobutene exhibits an olefinic proton peak at τ 4.03 and methylene resonance at τ 7.46, $J = 0 \pm 0.2$ Hz).[26] As a possibility, structure **29b** is photochemically sound[22] and might be considered consistent with the physical data described above; however, thermal conversion to starting benzenoid material of **29b** or of its valence tautomer, tri-*tert*-butylfulvene, seems unlikely.[29] Structure **29c** appears even less plausible, both on the grounds of photochemical improbability as well as expected nonreversion to aromatic recursor. Thus anticipated structure **28** remains as the most acceptable of the various candidates.

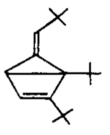
Table I

Peak, τ, ppm	Area	Spin–spin splitting	Assignment
3.87	1	Singlet, with minor shoulders	>C=C< H
3.95	1	Doublet (J = ~1.0 Hz)[b]	>Ċ=C< H
6.80	1	Doublet (J = ~1.0 Hz)[b]	>C—H
8.94	9	Singlet	*tert*-C_4H_9
9.02	18	Singlet	2*tert*-C_4H_9

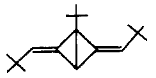
[a] Spectrum obtained on a 60-MHz Varian instrument using a carbon tetrachloride solution at room temperature. Values relative to tetramethylsilane (τ = 10.0). [b] As evidenced by the irregular nature of each of these two peaks, secondary splitting is also involved, probably between the lowest field proton with each of the other non-*tert*-butyl hydrogens.



29a

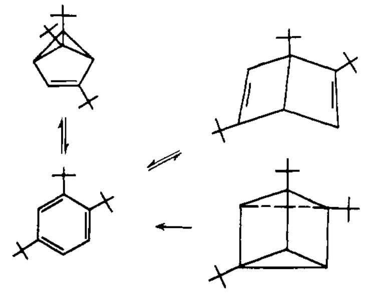


29b



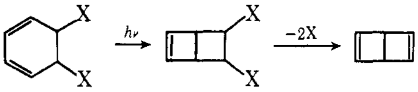
29c

Under different irradiation conditions, there are formed in detectable amount the other two valence bond isomers of 1,2,4-tri-*tert*-butylbenzene, structural assignments which are based on both chemical and spectral properties. Extended studies of the reaction system have led to the proposal of the following photochemical relationships.[23]



Uncovering of the tri-*tert*-butylbenzene–tri-*tert*-butyl-(Dewar benzene) interconversion served as an impetus for a sustained and intensified effort to produce the parent Dewar benzene case. The synthesis route to the C_6H_6 case, followed from the initiation of the project, was based on Scheme I. Because of the stereoelectronic considerations (*vide supra and infra*), existence of one, relatively thermally stable, cyclobutene moiety in the last intermediate was regarded as highly desirable, in that this structural feature would offer some insurance against formation of ordinary benzene in the last step. In view of the necessary provisions for generation of a new olefinic bond in the second, fused cyclobutene ring, a penultimate substance possessing already the carbon skeleton of the end product promised to be most useful. Also, the final step—conversion to Dewar benzene—should, in view of the expected sensitive nature of the sought hydrocarbon, be carried out under the mildest possible conditions with respect to temperature, pH, and nature of the reagent.

Scheme I



Initial attempts to reduce Scheme I to practice involved ultraviolet irradiation of *cis*- or *trans*-1,2-dihydrophthalic acid (**30**), readily obtained by sodium amalgam–acetic acid reduction of 1,2-phthalic acid.[30]

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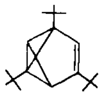
(26) K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961).

(27) Although it does not contain the two double bonds apparently demanded by nmr data, structure i, a novel yet reasonable irradiation possibility, warranted attention at this stage of the investigation. The values given by K. B. Wiberg and R. P. Ciula (*ibid.*, **81**, 5261 (1959)) for the ring protons in ethyl bicyclo[1.1.0]butane-1-carboxylate (ii) (H_a, 8.03; H_b 7.68 and 8.94) are not, however, in line with the critical two in our case, one of which falls at far lower fields; *cf.* I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *ibid.*, **90**, 5868 (1968).



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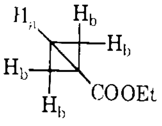
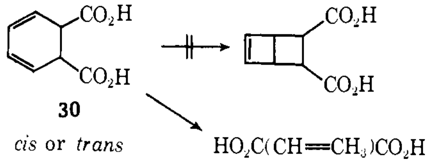


ii

(28) G. L. Cioss and L. E. Closs, *ibid.*, **83**, 1003 (1961); G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

(29) J. H. Day, *Chem. Rev.*, **53**, 179 (1953).

(30) A. Baeyer, *Ann.*, **269**, 145 (1892).

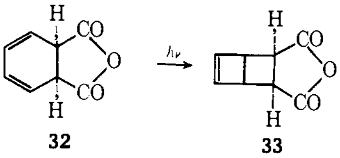


30
cis or *trans*

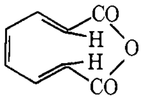
31

Periodic ultraviolet spectral analysis of the reaction mixture showed in each case development, and subsequent disappearance, of a 300-mμ bond, ending with mere end absorptions (except for a shoulder at 270 mμ). Chromatographic analysis of the reaction product revealed a complex mixture, which was not separated into individual components. On the basis of the above observations, it was conjectured that the dihydrophthalic acid suffered initial ring opening to the triene diacid (**31**), followed by further change of that product.

In order to avoid the undesired ring-opening reaction and to realize instead the required conversion to a bicyclo[2.2.0]hexene, we employed a simple chemical device: conversion of the dihydrophthalic acid to a cyclic derivative, *viz.* the *cis*-succinic anhydride (**32**), which would be comparatively loath to undergo a 1,3-cyclohexadiene 1,3,5-hexatriene ring opening. Although it would not have been possible at this time to predict with certainty the stereochemistry of photoinduced ring cleavage, it was evident that *any* nine-membered, triply unsaturated cyclic anhydride would be distinctly strained, and on that basis, a less likely photoproduct than the desired tricyclic anhydride (**33**). In the case of the potential trans,cis,trans anhydride, **34**, the 3,8-hydrogen steric interaction would be expected to destabilize the structure; in the (planar) all-cis structure **35**, bond angle distortion in the polyene system would be significant; and in the trans,cis,cis case, **36** internal strain would also be an important factor. In light of the presently established and accepted body of knowledge, ring opening would be expected[31] to lead to cyclic anhydride (**36**).



32 **33**



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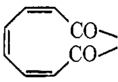

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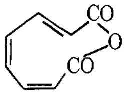
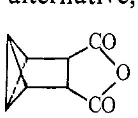


36

In the event, ultraviolet irradiation by means of a Hanovia lamp (Vycor filter) of *cis*-1,2-dihydrophthalic anhydride in ether readily produced a new, isomeric anhydride, which after sublimation and recrystallization appeared as fine needles (mp 162–163°). In the ultraviolet region of the spectrum, only end absorption was observed (>215 mμ), while the infrared spectrum featured normal succinic anhydride carbonyl (5.4 and 5.6 μ) and cis olefinic (13.3 μ) absorption. Molecular weight determination (150, mass spectrophotometric; 161 and 166, Rast) indicated the new substance to be monomeric. The photoanhydride could be hydrolyzed to a diacid (mp 205–207°), which was convertible at 100° to starting anhydride. On catalytic reduction, the new anhydride consumed 1 mol of hydrogen, and there was produced a saturated dihydro product (mp 85–86°) which did not possess a *C*-methyl group (nmr). The nmr spectrum of the photoanhydride displayed three peaks, all extensively split, at τ 3.51, 6.34, and 6.58 (CCl_4 solution, 60 MHz) in the hydrogen ratio 1:1:1. The above observations support strongly the proposed structure (**33**) for the photoanhydride, and rule out the alternative, tetracyclic possibility, **37**.



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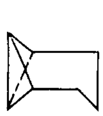
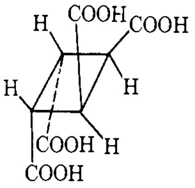


38

Thus, catalytic hydrogenation of anhydride **37** might be expected to produce a methylcyclopentane, in that such reduction converts the known bicyclobutane (**38**) to methylcyclohexane.[32] Also, the nmr behavior of the photoanhydride is not compatible with structure **37**, as a comparison with the known bicyclobutanes ii[27] and **38**[32] (τ 8.55, 8.33, and 7.58 in the ratio 6:2:2) reveals.

Finally, in a definitive degradation, the structure and stereochemistry of **33** were put on a secure basis.[33] Ozonolysis at −78° of the anhydride in ethyl acetate, followed by peracetic acid oxidation, provided in high yield *cis,trans,cis*-cyclobutane-1,2,3,4-tetracarboxylic acid (**39**), characterized as the tetramethyl ester.[34] In the reasonable assumption that no epimerization occurred during the oxidation sequence, the result confirms the gross structure of the photoanhydride and in addition establishes the stereochemistry of the anhydride ring as cis-fused and exo (**40**).



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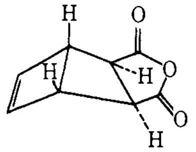

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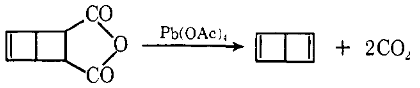
Oxidative decarboxylation of the photoanhydride to bicyclo[2.2.0]hexa-2,5-diene was achieved by several means. In the first trials with lead tetraacetate reagent, there was detected by vpc means a small amount of a hydrocarbon, which upon being heated in solution was converted to benzene. As our experience with the lead tetraacetate reaction broadened, there emerged a procedure which produced amounts of the new hydrocarbon adequate for structural study and assignment. Under rigorously controlled conditions (*inter alia:* reaction temperature 43–45°, bath 47–48°; 20-min reaction time; reduced pressure) the anhydride in pyridine solution was treated with the aforementioned reagent, while a minimal amount of distillate was collected in a



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(31) R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(32) W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

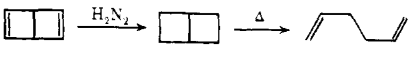
(33) The experimental chemistry described in this paragraph was carried out by D. Carty, Stanford University (Ph.D. Dissertation, 1967).

(34) R. Criegee and H. Hover, *Chem. Ber.*, **93**, 2521 (1960).

cooled receiver. Under these conditions a pyridine solution containing an amount of Dewar benzene representing an approximately 20% yield could be obtained.

Assignment of structure rests on the following observations. On being heated at 90° for 30 min, the new hydrocarbon in pyridine solution was converted quantitatively to benzene (analytical vpc); at room temperature the hydrocarbon in pyridine exhibits a half-life of about 2 days, again forming benzene. The benzene precursor itself can be successfully chromatographed in the vapor phase (Ucon polar column at 45°); its retention time (2.7 min) is of the order expected for a hydrocarbon in the C_6 range (cyclohexene = 3.3 min; bicyclo[2.2.0]hexane = 3.7 min; benzene = 5.7 min). Small amounts of material trapped from the vpc column exhibited only end absorption in the ultraviolet. The nmr spectrum, measured on a pyridine solution of hydrocarbon **4**, is reproduced herewith. The olefinic and methine protons, appearing in the ratio of 2:1, exhibit splitting with apparent $J = 0.7$ Hz for each interaction (see Figure 1). Olefinic hydrogen (τ 3.45) is split by the near as well as the far methine hydrogen, and thus appears as a triplet; in turn, methine hydrogen is acted upon by the four olefinic hydrogens and thus reveals itself as a qunituplet (τ 6.16). Thus the nmr data are consistent with structure **4**, and moreover constitute powerful support for the assignment.[35]

Substantiation by way of chemical behavior was found during the course of reduction experiments. Diimide (generated by decarboxylation of azodicarboxylic acid in the manner previously described[36]) hydrogenation of hydrocarbon **4** in pyridine-water-acetic acid solution was carried out. The product was identified as bicyclo[2.2.0]hexane (**41**), by comparison with an authentic sample[37a,b] as well as by pyrolysis to biallyl, known to be formed when bicyclo[2.2.0] is heated.[37a]



41

By means of preparative vpc methods, there was obtained a small amount of solvent-free, reasonably pure Dewar benzene, which was dissolved in carbon disulfide or tetrachloride, the resulting solution being used for measurement of the infrared spectrum (Figure 2). Notably different from the ir spectrum of benzene, the spectrum of Dewar benzene featured intense bands at 705 and 785 cm^{-1}, and a medium band at 825 cm^{-1}, ascribable to C-H out-of-plane deformations. Carbon–carbon double bond stretching is apparent from broad absorption in the 1400–1600-cm^{-1} region, and carbon–hydrogen stretching is revealed by bands in the 3000-cm^{-1} area.

Although the synthesis described above had served its purpose in leading to sufficient parent Dewar benzene for identification purposes, the lead tetraacetate decarboxylation reaction is capricious and difficult to scale up. In searching for a more satisfactory alternative, we learned that electrolytic decarboxylation of the photoacid proceeded smoothly and reliably, generating Dewar benzene in a ~35% yield as an easily isolable product.[38–43] As far as we are aware, this case represents the first application of succinic acid electrolytic decarboxylation to the formation of small ring compounds. In the procedure, the diacid is dissolved in aqueous pyridine–triethylamine, and the solution of amine salt is electrolyzed at room temperature with two platinum electrodes.[44,45] Extraction provides a Dewar benzene solution suitable for chemical or spectral study. Subsequent application of this synthetic method to other small ring or polycyclic cases is described elsewhere.[46]

After the synthesis and identification of representative bicyclo[2.2.0]hexa-2,5-dienes (Dewar benzenes) had

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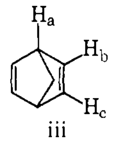
(35) An informative comparison case is norbornadiene (iii), in which $H_{a,b} = 2.9$; $H_{a,c} = 0.95$; and $H_{b,c} = 3.45 \pm 0.1$ Hz. F. S. Mortimer, *J. Mol. Spectrosc.*, 3, 528 (1959).



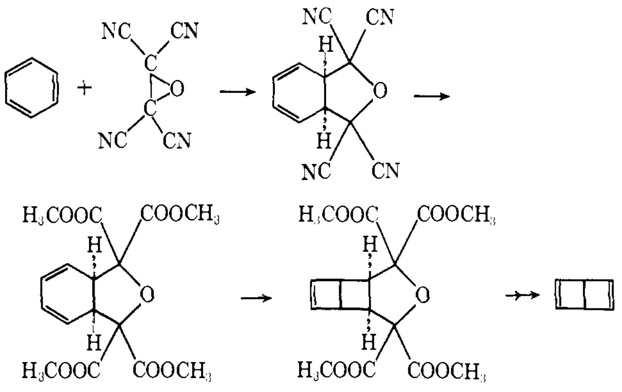
iii

(36) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Amer. Chem. Soc.*, **83**, 3725 (1961). See also E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Lett.*, 347 (1961); S. Hünig, H. R. Müller, and W. Thien, *ibid.*, 353 (1961).

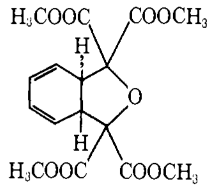
(37) (a) S. Cremer and R. Srinivasan, *Tetrahedron Lett.*, 24 (1960); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).

(38) This preparation of Dewar benzene was worked out (1965) by T. Whitesides, Stanford University, and was first disclosed (ref 4) in a Communication to the Editor by E. E. van Tamelen and D. Carty, *ibid.*, **89**, 3922 (1967).

(39) In a search for a method of converting, overall, benzene to Dewar benzene, the following scheme was pursued. The benzene–tetra-



cyanoethylene oxide adduct (1:1), obtained as previously described,[40] was converted directly to the tetramethyl ester by treatment with methanolic hydrogen chloride. Upon being irradiated in ethanol, the tetraester was transformed into a new substance with a similar chromophore, consistent with the observed rapid reduction of the starting 256-mμ peak to a lower intensity peak at the same wavelength, followed by no further change. On the basis of the uv, nmr, and mass spectra of the crystalline product, the structure iv was proposed. Presumably the trans-fused diene results from initial photoring opening to the cyclic *cis,cis,trans*-triene v, followed by thermal closure, a well-precedented



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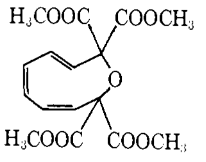


v

overall change.[41] (This synthetic approach was investigated by Drs. R. Magid and G. Parry, Stanford University.)

(40) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **85**, 2032 (1963).

(41) A. Windaus and G. Zuhlsdorff, *Justus Liebigs Ann. Chem.*, **536**, 204 (1938).

(42) R. Fichter, *Helv. Chem. Acta*, 24, 549 (1941).

(43) E. A. Pasquinelli, *An. Asoc. Quim. Argent.*, 31, 181 (1943).

(44) E. J. Corey and J. Casanova, Jr., *J. Amer. Chem. Soc.*, **85**, 165 (1963).

(45) H. Plieninger and W. Lehnert, *Chem. Ber.*, 100, 2427 (1967).

(46) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968).

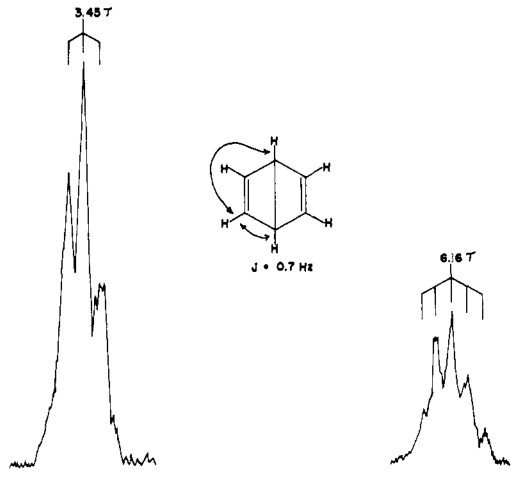
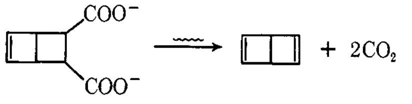
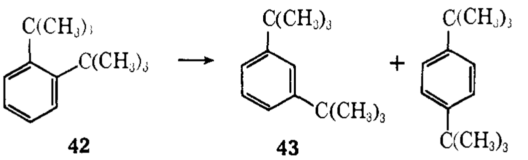


Figure 1. Nmr spectrum of Dewar benzene.

been achieved, efforts were made to extend the preparative methods, both of which relied upon photochemical assistance, to additional cases. Although in none of the experiments described below did a Dewar benzene, or reasonable precursor thereof, result, the changes encountered were in all cases novel at the time and are presented here in that light.



Since 1,2,4-tri-*tert*-butylbenzene, on ultraviolet irradiation, is transformed into the Dewar benzene counterpart, it might reasonably be expected that the simpler case, *o*-di-*tert*-butylbenzene (**42**), would in its behavior parallel that of the original example. However, no Dewar benzene could be identified as a product when the photolysis was conducted under conditions similar to those employed for the more complicated, earlier system. Instead, there was isolated, after irradiation of starting material in ether solution with a Hanovia type L lamp (Vycor filter), a mixture of *m*-di-*tert*-butylbenzene (**43**) (25.5% yield), *p*-di-*tert*-butylbenzene (**44**) (11.5% yield), and 8.5% *o*-di-*tert*-butylbenzene, which mixture was separated and analyzed by means of vapor-phase chromatography. The meta and para isomers were compared with authentic specimens, prepared simultaneously by alkylation of benzene with *tert*-butyl alcohol.[47] This experimental result suggested the existence of a photochemical equilibrium between at least two of the di-*tert*-butylbenzene isomers, and in fact on irradiation of either the meta or the para isomer under the conditions described above, the same mixture (58% para and 42% meta) was produced in 23–27% yield. In no case was there evidence for the formation of (mono) *tert*-butylbenzene or tri-*tert*-butylbenzene.[48,50]



42 **43** **44**

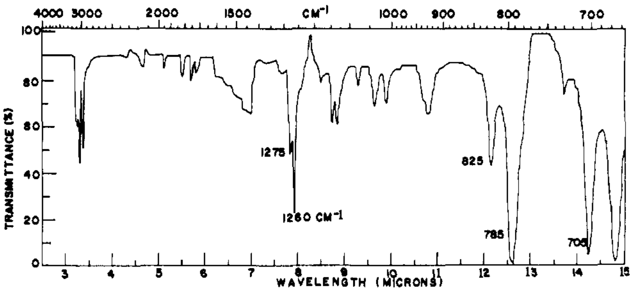


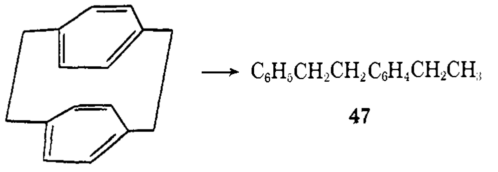
Figure 2. Infrared spectrum of Dewar benzene.

It was suggested[48] early that the isomerization reaction might involve actual alkyl transfer, but could equally well proceed through benzene valence bond isomers, *e.g.*, benzvalenes, which could suffer bond cleavage in such a way as to generate, not the aromatic progenitor, but isomeric benzenoids. This course of events was established and delineated by Wilzbach and Kaplan who showed in fact that a benzvalene (**45**)

45

is an intermediary type.

X-Ray diffraction[51] and ultraviolet[52] studies have revealed ring distortion in the smaller paracyclophanes, which phenomenon implies unusual behavior in product development during irradiation. After being photolyzed (Corex filter, Hanovia lamp) in hexane solution for 12 hr, [2.2]paracyclophane (**46**)[52,53] generated a 37% yield of 1-*p*-ethylphenyl-2-phenylethane (**47**), identical with authentic material.[54] In addition, 20% of the starting material was recovered, and an inseparable mixture of low R_f (tlc) hydrocarbons was encountered. In ether solution, a similar array of products was formed, along with three substances each of which contained one (ir, nmr, and ethoxyl analysis) ethoxyl group. In no case was there indication of valence bond isomer formation.[55]



46 **47**

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(47) H. Meyer and K. Bernhauer, *Monatsh.*, **53–54**, 726 (1929).

(48) The di-*tert*-butyl irradiation observations described herein appear in the University of Wisconsin Ph.D. Dissertation (1963) of K. L. Kirk and were first presented publicly in an American–Swiss Foundation Lecture by E. E. van Tamelen in Zürich on May 8, 1964. The results are in substantial agreement with those obtained subsequently by Burgstahler and Chien, with whom we had been in correspondence on this subject prior to the submission of their manuscript.[49]

(49) A. W. Burgstahler and P.-L. Chien, *J. Amer. Chem. Soc.*, **86**, 2940 (1964).

(50) An extensive mechanistic study of the photoisomerization of polyalkylbenzenes has been made by L. Kaplan and K. E. Wilzbach, *ibid.*, **86**, 2307 (1964), and succeeding references.

(51) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

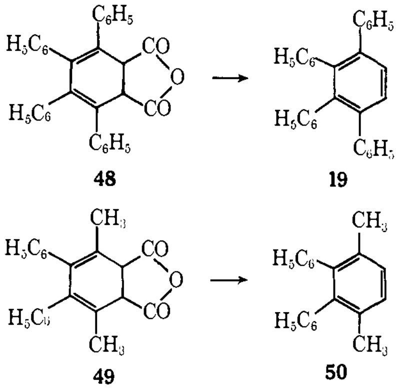
(52) D. J. Cram and L. Singer, *J. Amer. Chem. Soc.*, **85**, 1075 (1963).

(53) H. Wynberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

(54) C. Söllscher, *Chem. Ber.*, **15**, 1681 (1882).

(55) These results (K. Kirk, Ph.D. Dissertation, University of Wisconsin, 1963), are similar to those obtained using a different (methanol) solvent system: R. C. Helgeson and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 509 (1966).

Because of stability and other considerations, syntheses of substituted Dewar benzenes were desired, and it was hoped that the parent Dewar benzene synthesis described above could be applied to more complex anhydrides. For these reasons, attempts were made to convert by ultraviolet irradiation the cyclohexa-1,3-dienes **48** and **49** to the substituted bicyclo[2.2.0]hexenes, corresponding to **40**. However, in each case, the major product isolated turned out to be the substituted aromatic resulting from loss of the anhydride function, presumably as carbon monoxide and carbon dioxide. Photolyses were conducted for 1 hr, using dioxane solutions of anhydrides, and a Hanovia lamp equipped with a Vycor filter. Under these conditions, the yield of 1,2,3,4-tetraphenylbenzene (**19**) from **48** was 34%, while 1,4-dimethyl-2,3-diphenylbenzene (**50**) was generated in 81% yield. In both cases, significant amounts of starting material were accounted for; in neither case could any evidence for cyclobutene ring formation be uncovered.[56,57]



Two elements of the above Dewar benzene chemistry deserve elaboration: the photochemical formation and the thermal stability of the Dewar benzene system. Since the initial appearance[1] and subsequent partial theoretical discussion[11] of our work, various other laboratories have substantiated, extended, and further discussed this area of chemistry, and the ensuing interpretations represent the best views on the subject at the present time.

Because the stability of Dewar benzenes was, when first observed, surprising, comment on this property is called for. In an earlier section of this paper, certain reasons for predicting isolation and retention of a Dewar benzene were presented, and we now consider the theoretical aspects of these points. Two thermodynamic factors, namely the strain of Dewar benzene and the resonance stability of Kekulé benzene, reinforce each other and suggest a considerable difference in the ground-state energies of the two structures. Furthermore, the shapes of the two isomeric systems are similar, so that the skeletal reorganization needed for aromatization of Dewar benzene is minimal. The above factors alone would suggest an energy profile featuring a largely downhill path (Figure 3, ---). In order to explain the observed order of stability, we must look to the electronic factors operative in the thermal conversion of a cyclobutene to a 1,3-diene. The stereochemical behavior of substituted cases, described above, has been interpreted[31,58–60] in terms of the highest occupied molecular orbital of the electronic system. In the case of Dewar benzene, the preferred thermal mode of ring-opening (conrotary) **51** cannot operate, since an extraordinarily strained *cis,cis,trans*-cyclohexa-1,3,5-diene (**52**) would result. Because of this stereoelectronic barrier to aromatization, Dewar benzene is therefore more thermally (Figure 3,—) stable than it otherwise would be, and sufficiently so to permit isolation in many cases.[61] Also, these same forces are at work in the synthesis of parent Dewar benzene, and permit retention of the cyclobutene system in the final reaction, which leads to the Dewar benzene system.

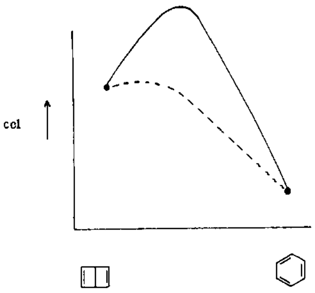
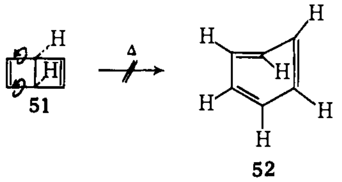


Figure 3.



The conversion of 1,2,4-tri-*tert*-butylbenzene to the Dewar counterpart, described above, was the first example of the photochemical conversion of a benzenoid to the corresponding isolable valence bond isomer, and has been succeeded by a variety of other examples. The photochemistry involved in this case is complicated by an additional effect, the steric interaction of the 1,2-di-*tert*-butyl groups. As indicated by exaltation of diamagnetic susceptibility,[62a] *o*-di-*tert*-butylbenzene and 1,2,4-tri-*tert*-butylbenzene possess ~70% of the normal aromaticity, and thus would be expected to reveal abnormal photolytic behavior. As suggested by X-ray results obtained with 1,2,4,5-tetra-*tert*-butylbenzene,[62b] the 1,2,4-tri-*tert*-butylbenzene case should be planar but suffer from bond angle distortions (α and α') in the ortho-substituted moiety, **53**. According to the results of Ishikawa and Noyes,[63] who studied benzene itself, the first photochemical event in the ultraviolet irradiation of aromatic **27** would be conversion to the

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(56) Experimental results secured by R. Magid, Stanford University, 1964.

(57) R. N. Warrener and J. B. Bremner (*Tetrahedron Lett.*, 5691 1966)) reported photolytic conversion of anhydride **48** to 1,2,3,5-tetraphenylbenzene and a trace of the 1,2,3,4 isomer, at 25°, while at −10° 1,2,3,4-tetraphenylbenzene is formed from this same anhydride (R. Kitzing and H. Prinzbach, *Helv. Chim. Acta*, **53**, 158 (1970)).

(58) L. J. Oosterhoff, as quoted in E. Havinga and J.L.M.A. Schlatmann, *Tetrahedron*, **16**, 151 (1961).

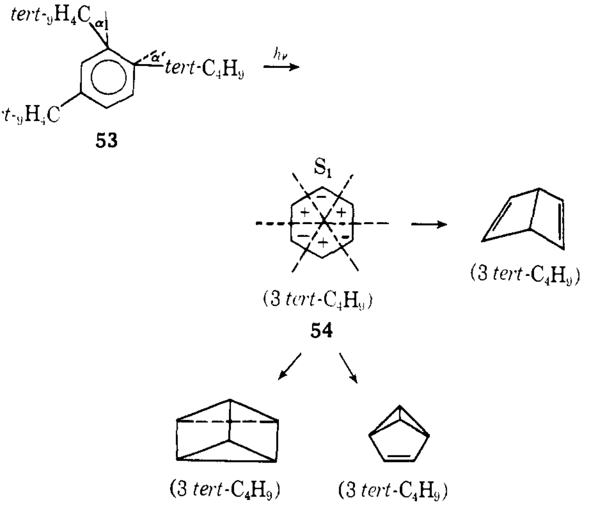
(59) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(60) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(61) This view was originally expressed by us in 1965 (ref 11) and is supported by R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(62) (a) Footnotes 66 and 77 and (b) footnote 74 in E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967).

(63) H. Ishikawa and W. A. Noyes, Jr., *ibid.*, **84**, 1502 (1962).



first excited singlet, with B_{IU} symmetry (**54**).[64] Among the many reaction courses open to the S_1 species,[65] transformations to valence bond isomeric systems are included, with Dewar benzenes, prismanes, and benzvalenes being Woodward–Hoffmann permitted.[61] Under the conditions used in our laboratory, including minimal irradiation time, conversion to the Dewar structure seems to be preferred kinetically to isomerization to the prismane or benzvalene. The geometrical change in the carbon skeleton characterizing the formation of the Dewar benzene is accompanied by loss or diminution of the steric interference destabilizing the ground and excited aromatic.[66]

Experimental Section

Melting points are uncorrected and taken in open capillaries in a Hershberg apparatus, unless otherwise stated. The infrared spectra were measured on a Baird infrared recording spectrometer (Model B) with 0.1-mm cells. A Cary recording spectrophotometer (Model 11MS) was used to measure the ultraviolet spectra (1-cm quartz cells in 95% ethanol, unless otherwise stated). The solvents used were either of reagent grade quality or purified by standard methods.

1,2,5-Tri-*tert*-butylbicyclo[2.2.0]hexa-2,5-diene (28). 1,2,5-Tri-*tert*-butylbenzene (200 mg) was irradiated in 1 l. of ether solution, into which was immersed a quartz-jacketed water condensor with an inner well containing a Vycor filter and immersion light source (Hanovia, type L). As the photolysis proceeded, the solution was stirred both by nitrogen ebullition and magnetically, and samples were withdrawn every 0.25 hr for ultraviolet spectral studies. The solution was photolyzed for 2.5 hr, during which time the ultraviolet spectra changed very rapidly, and then remained constant for 2 hr. The initial band at 266 mμ had shifted to 260 mμ and increased in intensity by fivefold, while the shoulder at 217 mμ had disappeared and the extinction at that wavelength had decreased by twofold.

The pale-yellow ether solution was concentrated, and the crude product was analyzed by thin-layer chromatography using silica gel and petroleum ether. The faster moving spot (R_f = ~0.7) possessed only end absorption in the ultraviolet (ε 1800 at 220 mμ). The ultraviolet spectrum of the other spot (R_f = ~0.5) was similar to that of the crude product, λ_{max} 260 mμ (ε 1200).

The crude product from the photolysis (150 mg) was spotted along the bottom of three plates (200 × 200 mm) with the silica gel approximately 0.6 mm thick. Using cyclohexane as the liquid phase, 30 mg (20%) of fast moving material, a clear oil, and 45 mg (30%) of slow moving substance, a bright yellow oil, were isolated. The nuclear magnetic resonance and infrared spectra ($\lambda_{max}^{CCl_4}$ 6.26 and 6.46 mμ), as well as the molecular weight determination[25] of the clear oil, were obtained without further purification. The mass spectrum[24] and elemental analysis were obtained after the oil was distilled at room temperature with a mercury diffusion pump (10^{-7} mm). This purified material was crystalline below 0°.

After pyrolysis of 9 mg of the fast moving spot in 2 ml of carbon tetrachloride in a sealed tube for 15 min at 200°, the starting aromatic, 1,2,4-tri-*tert*-butylbenzene (6 mg), was isolated by sublimation of the crude product at 40° (1.0 mm). A mixture of this material, mp 44–46°, and the starting material (mp 48–49°) melted at 45–47°.

Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27; mol wt, 246. Found: C, 87.47, 87.52; H, 12.22, 12.31; mol wt, 274.

Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic Anhydride (33). 1,2-*cis*-Dihydrophthalic anhydride, 2.7 g,[30] was irradiated in 1 l. of ether with a Hanovia 450-W light source and Vycor filter sleeve contained in a quartz immersion well. During the course of irradiation, nitrogen was passed through the solution and aliquots were analyzed by ultraviolet spectral determinations. During this time, the absorption bands of the starting anhydride (λ_{max}^{ether} 264 (ε 4.8 × 10^3) and 256 mμ (ε 5.0 × 10^3)) diminished and end absorption (at 220 mμ) increased. After 4.5-hr irradiation, the solution was concentrated and the product sublimed at 50° (0.03 mm). The sublimate, 760 mg, was crystallized from hexane to afford 600 mg (22%) of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride, mp 162–163°. The ultraviolet spectrum exhibited only end absorption; anhydride carbonyl (5.4 and 5.6 μ) and cis olefinic (13.3 μ) absorptions were features of the infrared spectrum. The nmr spectrum exhibited finely split multiplets of equal intensity at τ 3.51, 6.34, and 6.58.

Anal. Calcd for $C_8H_6O_3$: C, 64.00; H, 4.03; mol wt, 150. Found: C, 64.08; H, 3.96; mol wt, 150 (mass spectral); 161, 166 (Rast).

Bicyclo[2.2.0]hexa-2,5-diene (4). The bicyclic anhydride (200 mg) was dissolved in 10 ml of pyridine in a 25-ml three-necked flask, equipped with a thermometer immersed in the solution, and a 145° curved adapter which was connected *via* a straight vacuum take-off adaptor to a collection flask. The adaptors were wrapped with glass wool. The system was alternately evacuated (water aspirator) and filled with N_2 several times. On addition of lead tetraacetate (1 g) the reaction flask was immersed in an oil bath at 48°; the collection flask was immersed into a Dry Ice–acetone slurry. The temperature of the solution was held between 43 and 45° by adjusting the vacuum (water aspirator) with an N_2 bleed. The reaction was allowed to proceed for 30 min; during this time 1 ml of distillate was generally collected, although this volume varied from 0.5 to 2 ml. In addition to benzene, the pyridine distillate invariable contained a single volatile component (by glc) which was ultimately shown to be bicyclo[2.2.0]hexa-2,5-diene, although the yield of this material was found to be highly variable (5–20%). The product exhibited a retention time of 8 min on glc (Perkin-Elmer 154-D vapor fractometer) utilizing a 150-ft polar Golay column at 40°. Under these conditions the retention times of cyclohexene and benzene were 9 and 17 min, respectively. On heating the pyridine solution at 90° for 30 min the product was converted into benzene (determined by glc). At room temperature, the product exhibited a half-life of about 2 days, again forming benzene. The product was shown to exhibit only end absorption in the ultraviolet spectrum by collection (liquid nitrogen trap) from a gas chromatography column (packed with Gas Chrom P, available from Applied Science Laboratories, Inc., on which was absorbed Ucon Polar, 20% by weight, available from Wilkins Instrument and Research, Inc.) when the detector was bypassed. Passage through the thermal detector resulted in the conversion to benzene. The identities of the product and benzene were confirmed by subsequent glc analysis of the trapped substances.

The nmr spectrum of the product in pyridine exhibited a triplet at τ 3.45 (J = 0.7 Hz) and a quintuplet at 6.16 (J = 0.7 Hz) in the ratio of 2:1.

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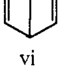
(64) S. F. Mason, *Quart. Rev., Chem. Soc.*, **15**, 287 (1961).

(65) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(66) Two two-dimensional expressions have been used to symbolize Dewar benzene: vi and vii. The first has obvious chemical historical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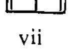
vii

origins,[8] whereas it is perhaps not as widely known that vii has long served as the brand of the western USA Bible Ranch. Although vii might be considered as the preferable representation of a bicyclo[2.2.0]-hexa-2,5-diene, vi has the virtue of emphasizing the length of the 1,4 bond—in the case of hexamethyl(Dewar benzene), apparently the longest single bond (1.63 Å) on record (M. J. Cardillo and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 2399 (1970)).

Diimide Reduction of Bicyclo[2.2.0]hexa-2,5-diene. To a pyridine solution (100 μl) of the bicyclohexadiene in a small flask was added 300 mg of dipotassium azodicarboxylate followed by 500 μl of acetic acid. The mixture became a solid mass and, after 3 hr, 200 μl of water was added. The product was shown to be identical with an authentic sample of bicyclo[2.2.0]hexane[37] by glc utilizing two columns and various conditions including mixture of the reduction product with the known bicyclohexane.

The reduction was also carried out by adding dipotassium azodicarboxylate (100 mg) to a solution of water, 400 μl, and pyridine, 100 μl, containing the bicyclohexadiene. Subsequently, acetic acid was added in three 400-μl portions over a period of 2 hr. Half of the resulting solution was swirled with decalin, 200 μl, and the organic layer was pyrolyzed in a sealed tube at 200° for 20 min. The resulting product was shown to be identical (glc) with authentic 2,5-hexadiene, known to be formed from the pyrolysis of bicyclo-[2.2.0]hexane.[37b]

The Hydrolysis of Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic Acid Anhydride (33). The photoanhydride (93 mg) was suspended in 2 ml of water containing a drop of phenolphthalein solution, cooled in an ice bath, and stirred magnetically. Sodium hydroxide (3 *N*) (0.4 ml) was added dropwise, after which the mixture became clear and remained pink. Then 10% hydrochloric acid (0.4 ml) was added. The resulting clear solution was extracted with ether, which was subsequently washed with saturated sodium chloride solution and dried over sodium sulfate. The ether extract was concentrated on the steam bath to afford 85 mg of white crystals (mp 205–207°) with end absorption in the ultraviolet at 220 mμ (ϵ 400). On sublimation at 100° (0.03 mm), the diacid reverted to the starting photoanhydride, which was readily collected from the cold finger.

Irradiation of *o*-Di-*tert*-butylbenzene (42). Using the procedure described for the irradiation of 1,2,4-tri-*tert*-butylbenzene, 200 mg of *o*-di-*tert*-butylbenzene was irradiated in 1 l. of anhydrous diethyl ether (Vycor filter). The reaction was followed by removing 1.0-cm^3 aliquots periodically for ultraviolet spectral analysis. After 2.75 hr the spectrum remained constant. During the reaction the extinction of the original maximum at 262 mμ increased by a factor of 4.4, and an additional peak of equal intensity appeared at 225 mμ. The end absorption at 220 mμ decreased by a factor of 1.5. The solvent was removed under aspirator vacuum; the yellow residue was dissolved in a small amount of ether and spotted on 8.10 × 20 cm silica gel thin-layer chromatography plates. Elution with hexane resulted in the separation of the crude reaction mixture into four product fractions, with R_f values of 0.70 (3.0 mg), 0.62 (11.4 mg), 0.55 (48.3 mg), and 0.48 (31.7 mg). In addition, 22.3 mg of material remained at the origin.

The ultraviolet spectrum of the fastest moving product showed only end absorption, λ^{Et_2O} 220 mμ (ϵ 1600). In the nuclear magnetic resonance spectrum there were sharp singlets of equal intensity at τ 9.03 and 8.94. A sample of this material (*ca.* 1 mg) was heated in a sealed tube in 1 cm^3 of carbon tetrachloride solution at 200° for 15 min. Thin-layer chromatography (silica gel–hexane) of the pyrolysate showed the absence of the material with an R_f value of 0.70. Attempts to detect *o*-di-*tert*-butylbenzene as a product of the pyrolysis by thin-layer and vapor-phase chromatography were unsuccessful.

In the nuclear magnetic resonance spectrum of the second thin-layer fraction, R_f = 0.62 (11.4 mg), singlets were present at τ 8.70, 8.68, 2.92, and 2.82, and a multiplet was centered at 2.72. The ratio of high-field to low-field protons was 18:4. The ultraviolet spectrum exhibited normal aromatic absorption: $\lambda_{\max}^{Et_2O}$ 261 (248), 262 (322), 254 (311), 249 (295), 243 mμ (277). Vapor-phase chromatography on a 2-m silicone column at 180° showed peaks corresponding to 42% *m*-, 66% *p*-, and 2% *o*-di-*tert*-butylbenzene.

The nuclear magnetic resonance spectrum of the third thin-layer fraction, R_f = 0.55 (48.3), showed singlets at τ 8.68 (18 protons), 2.92, 2.82, and a multiplet at 2.72, with a total of four low-field protons; ultraviolet spectrum, $\lambda_{\max}^{Et_2O}$ 270 (196), 260 (369), 254 (345), 249 (306), 244 (217). Vapor-phase chromatography under the conditions used above showed peaks corresponding to 61% *m*-, 27% *p*-, and 2% *o*-di-*tert*-butylbenzene. A sample of the peak corresponding to the para isomer, collected by preparative vapor-phase chromatography, mp 78.5–80.2°, showed no melting point depression when mixed with authentic material. A sample corresponding to the meta isomer was similarly collected and proved to be identical with authentic material with respect to ultraviolet and nuclear magnetic resonance spectra.

Table II. Ultraviolet Spectral Changes During Irradiation of [2.2]Paracyclophane (Vycor Filter, 3.5 hr)

[2.2]Paracyclophane $\lambda_{\max}$, mμ	 ϵ	Crude product $\lambda_{\max}$, mμ	 ϵ
305 (s)	130	273	615
287	212	267	715
225	19,000	264	785
		259	873
		220	18,000

Singlets at 8.70 (7.4 protons) and 8.48 (10.6 protons) and low-field absorption from 2.45 to 3.15 (4 protons) were present in the nuclear magnetic resonance spectrum of the fourth thin-layer fraction, R_f = 0.48 (31.7 mg); ultraviolet spectrum, $\lambda_{\max}^{Et_2O}$ 261 (367), 255 mμ (364). Vapor-phase chromatography showed the mixture to be made up of 41% *m*-, 7% *p*-, and 52% *o*-di-*tert*-butylbenzene.

The yields, calculated from the vapor-phase chromatography peak area and based on 200 mg of starting material, were 25.5% *m*-, 11.5% *p*-, and 8.6% *o*-di-*tert*-butylbenzene.

Irradiation of *m*-Di-*tert*-butylbenzene. A 7-mg sample of *m*-di-*tert*-butylbenzene was irradiated in 350 cm^3 of ether for 1 hr (Vycor filter). The crude product, obtained by removal of the ether under aspirator vacuum, was separated by preparative thin-layer chromatography (silica gel–hexane). A 1.6-mg (24%) fraction was obtained consisting of 58% *m*- and 42% *p*-di-*tert*-butylbenzene, identified by vapor-phase chromatographic analysis.

Irradiation of *p*-Di-*tert*-butylbenzene. A 90-mg sample of *p*-di-*tert*-butylbenzene was irradiated for 1 hr in 1 l. of ether (Vycor filter). One-fourth of the crude product, obtained by removal of the ether under aspirator vacuum, was separated by preparative thin-layer chromatography (silica gel–hexane). A fraction was obtained, 6.2 mg (27%), made up of 58% *p*-, and 42% *m*-di-*tert*-butylbenzene.

Irradiation of [2.2]Paracyclophane (46). [2.2]Paracyclophane was prepared by the method of Winberg.[53] Purification by recrystallization from acetic acid gave white crystals, mp 285–286.2° (sealed tube) (lit.[52] mp 285–287°). Irradiations were done in diethyl ether (Vycor and Corex filters) and in hexane (Corex filter).

Irradiation in Ether (Vycor Filter). In the initial experiment, 315 mg of [2.2]paracyclophane was dissolved in 1 l. of ether and irradiated for 3.5 hr. Aliquots were taken for periodic ultraviolet spectral analyses (Table II). At the end of the reaction, the ether was removed under aspirator vacuum to give 386 mg of partially crystalline oil. Trituration with ether and filtration gave 32 mg of starting material, mixture melting point with authentic sample undepressed. A 213-mg sample of the residue was dissolved in chloroform and chromatographed over 14 g of silica gel. Elution with 10% chloroform in petroleum ether gave 33 mg (20% based on 315 mg of **46**) of an aromatic hydrocarbon. The infrared, ultraviolet, and nuclear magnetic resonance spectra, as well as thin-layer chromatographic behavior (silica gel–benzene), were identical with the corresponding data of authentic 1-*p*-ethylphenyl-2-phenylethane (**47**). Further elution gave 14 mg of starting material, mixture melting point with an authentic sample undepressed. The total yield of recovered [2.2]paracyclophane was 18%. Continued elution with increasing concentrations of chloroform in petroleum ether gave 77 mg of a yellow oil, eluted with chloroform.

Under the same conditions as above, 300 mg of **46** was irradiated for 8.5 hr. Chromatography as before gave **47** in 5% yield, recovered [2.2]paracyclophane in 6% yield, a yellow oil in 27% yield, and a white solid in 32% yield.

Irradiation in Hexane (Corex Filter). Irradiation of 150 mg of [2.2]paracyclophane in 1 l. of hexane resulted in ultraviolet spectral changes similar to those observed in the irradiations in ether. Thin-layer chromatography showed the presence of two spots, corresponding to **47** and **46**. A 1:5 aliquot of the reaction mixture was separated by preparative thin-layer chromatography. **47** was obtained in 37% yield. Starting material was recovered in 20% yield.

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