

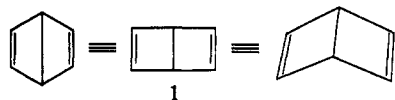
# Valence Bond Isomers of Aromatic Systems

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Received June 23, 1971

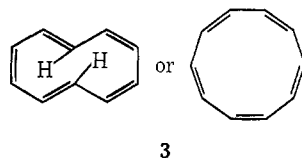
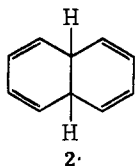
Preparation and identification of the first [2.2.0]-hexa-2,5-diene ("Dewar benzene") (1) was announced



in 1962.<sup>1,2</sup> During the ensuing years there were uncovered, both in our laboratory and elsewhere, a variety of other *valence bond isomers of aromatic systems*, many of remarkable structure and surprising stability. In this Account, we trace the main thread of our own endeavor, as it is now woven into the fabric of the work of others.

In view of the variety of known benzenoid, naphthalenoid, and other polycyclic aromatic types as well as heterocyclic, nonbenzenoid aromatic, and homoaromatic systems, the number of valence bond isomers of aromatic structures is virtually limitless, including mono-, bi-, and tricyclic versions of monocyclic ( $2 + 4n$ )- $\pi$ -electron parents. At the present time members of all three categories are known, although the most numerous are the monocyclic cases. Nomenclature systems have been suggested,<sup>3a,b</sup> and orbital symmetry aspects of the observed or hypothetical interconversions of aromatic and valence bond isomeric species have been discussed.<sup>3,4</sup>

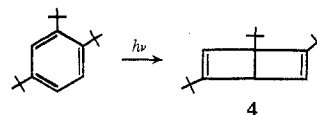
During the early 1960's we selected two aromatic valence bond isomer cases for study; the bicyclo-[2.2.0]hexa-2,5-diene ("Dewar benzene") system and the 9,10-dihydronaphthalene system (2), valence bond isomeric with the cyclodecapentaene type (3). By



1962, the preparation and characterization of 1,2,5-tri-*tert*-butylbicyclo[2.2.0]hexadiene (4) were complete,<sup>1</sup> and in the following year the synthesis and structure proof of parent "Dewar benzene"<sup>5</sup> and parent *cis*-9,10-

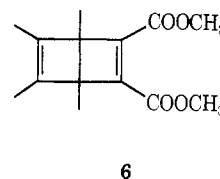
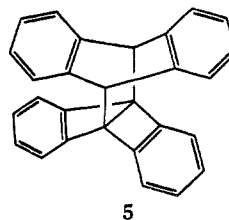
*Eugene E. van Tamelen, a native of Michigan, received the A.B. degree from Hope College in 1947, and the Ph.D. degree from Harvard in 1950. He rose through the ranks from instructor to full professor at the University of Wisconsin. Since 1962 he has been Professor of Chemistry at Stanford University and concurrently, since 1967, Professor Extraordinarius in the Netherlands.*

*Professor van Tamelen's research interests include organic synthesis, biosynthesis, biogenetic-type synthesis, nitrogen fixation, structure determination of natural products, photochemistry, and molecules of theoretical interest, including "Dewar benzene" and cyclodecapentaene. He is a member of the National Academy of Sciences and has been the recipient of various honorary degrees and national scientific awards.*



dihydronaphthalene<sup>6</sup> were reported. Concurrently there was observed<sup>7</sup> the photochemical interconversion of di-*tert*-butylbenzenes, behavior reflecting—as clearly and elegantly demonstrated later<sup>8</sup>—the role of benzene valence bond isomer phenomena at the excited-state level.

In the following year (1964) results from other laboratories began to appear, including the identification of four new Dewar benzene cases. Applequist and Searle described the "Dewar anthracene" 5, in which conversion to the parent anthracene is prohibited by reason of excessive angle strain in the latter structure.<sup>9</sup> Criegee and Zanker reported the synthesis of a tetramethyl Dewar phthalic ester (6), a substance—like our



earlier cases—of comparatively high stability.<sup>10</sup> Arnett and Bollinger obtained 1,2,3,5-tetra-*tert*-butyl(Dewar benzene) (7) by photoinduced valence bond *and* positional isomerization of 1,2,4,5-tetra-*tert*-butylbenzene.<sup>11</sup> Finally Viehe and coworkers described the trimerization of *tert*-butylfluoroacetylene to the trifluoro-tri-*tert*-butyl(Dewar benzene) 8.<sup>12</sup>

(1) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962).

(2) E. E. van Tamelen, Abstract, American Chemical Society 18th National Organic Symposium, Columbus, Ohio, June 1963.

(3) (a) E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965); (b) Z.A.T. Balaban, *Rev. Roumaine Chim.*, **11**, 1097 (1966).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(5) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

(6) E. E. van Tamelen and B. Pappas, *ibid.*, **85**, 3296 (1963).

(7) K. Kirk, Ph.D. Thesis, University of Wisconsin, 1963.

(8) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Amer. Chem. Soc.*, **87**, 675 (1965).

(9) D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

(10) R. Criegee and F. Zanker, *Angew. Chem.*, **76**, 716 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 695 (1964).

(11) E. M. Arnett and J. M. Bollinger, *Tetrahedron Lett.*, 3803 (1964).

(12) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem.*, **76**, 922 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964).

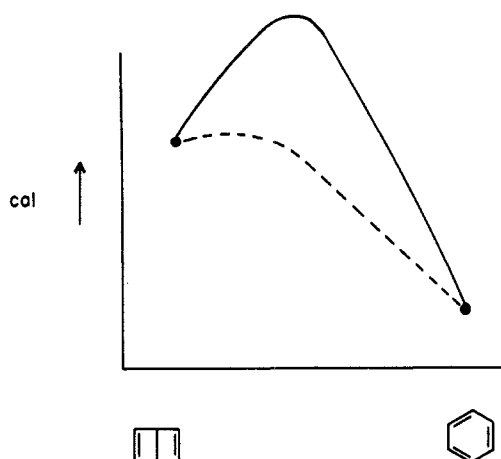
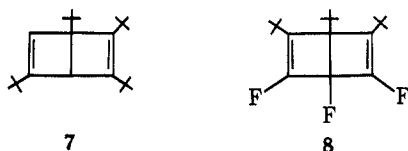
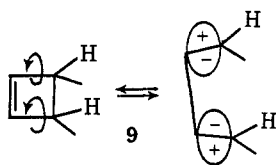


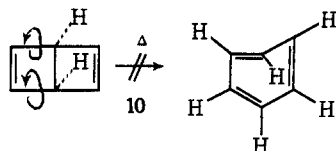
Figure 1.



Two theoretical aspects of Dewar benzene chemistry deserve comment: photochemical formation and thermal stability. The stability of Dewar benzenes was, at first sight, surprising, since two thermodynamic factors, namely the internal strain of Dewar benzene and the resonance stability of Kekulé benzene, would cooperate, guaranteeing a considerable difference in the ground-state energies of the two structures. Furthermore, the two isomeric systems are geometrically similar, and thus the skeletal reorganization needed for aromatization of Dewar benzene is minimal. If no other factors were at work, an energy profile featuring a largely downhill path would be anticipated (Figure 1, dashed line). Explanation of the stability of Dewar benzene can be found by considering the electronic factors operative in the thermal conversion of a cyclobutene to a 1,3-diene, interpreted in terms of the highest occupied molecular orbital of the diene system (9).<sup>4</sup> In the case of Dewar



benzene, this preferred, thermal mode of ring opening (conrotary) (10) cannot operate, since an extra-

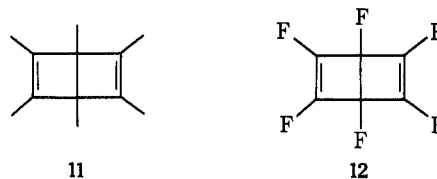


ordinarily strained *cis,cis,trans*-cyclohexa-1,3,5-triene would result.<sup>3a</sup> Because of this stereoelectronic barrier, Dewar benzene is therefore thermally aromatized more slowly (Figure 1, solid line) than might be expected on

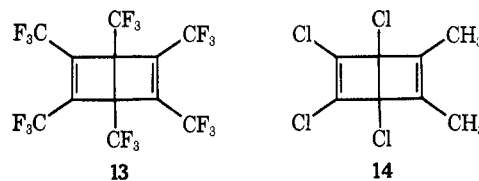
the basis of thermodynamic considerations alone, and sufficiently so to permit isolation in many cases.

The first photochemical event in the ultraviolet irradiation of benzene is transformation to the first excited singlet, with  $B_{1u}$  symmetry. Among the many reaction courses open to the  $S_1$  species, transformation to valence bond isomeric systems are included, with formation of Dewar benzenes, prismanes, and benzvalenes being Woodward-Hoffmann permitted. Under the conditions originally used in our laboratory, including minimal irradiation time, conversion of 1,2,4-*tert*-butylbenzene to the Dewar benzene 4 seems to be preferred kinetically to isomerization to the prismane or benzvalene. The geometrical change in the carbon skeleton involved in the formation of the Dewar benzene is accompanied by loss or diminution of the steric compressions which destabilize the ground and excited states of 1,2,4-*tert*-butylbenzene. Under other circumstances, including equilibration, the starting aromatic can provide varying amounts of benzvalene or prismane (*vide infra*).

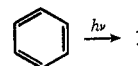
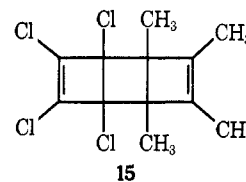
In more recent times, a variety of additional Dewar benzenes and related species have been created and characterized. Among these are: hexamethyl(Dewar benzene) (11), formed in good yield by  $AlCl_3$ -catalyzed



trimerization of butyne-2;<sup>13</sup> hexafluoro(Dewar benzene) (12)<sup>14</sup> and hexakis(trifluoromethyl)(Dewar benzene) (13),<sup>15</sup> photoproducts of the corresponding benzenoids; and 1,2,3,4-tetrachloro-5,6-dimethyl(Dewar benzene) (14), formed by photolysis of the ozonide from the mixed



cyclobutadiene dimer 15.<sup>16</sup> Meanwhile, parent Dewar



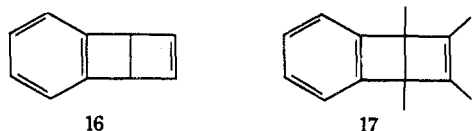
(13) W. Schäfer, *Angew. Chem.*, **78**, 716 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 668 (1966).

(14) (a) I. Haller, *J. Amer. Chem. Soc.*, **88**, 2070 (1966); (b) G. Cammagi, F. Gozzo, and G. Cedivalli, *Chem. Commun.*, 313 (1966); (c) A. Bergoni and F. Gozzo, *Chim. Ind. (Milan)*, **50**, 745 (1968).

(15) (a) D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, **91**, 3373 (1969); (b) M. G. Barber, R. N. Haszeldine and R. Hubbard, *Chem. Commun.*, 202 (1969).

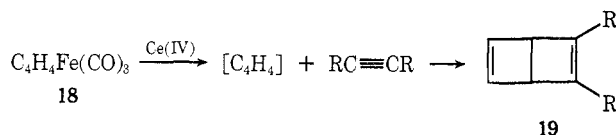
(16) R. Criegee and R. Huber, *Angew. Chem., Int. Ed. Engl.*, **8**, 759 (1969).

benzene was shown to derive from benzene itself, when the latter was photolyzed in the liquid phase.<sup>17</sup> In addition, Dewar naphthalenes **16**<sup>18</sup> and **17**<sup>19</sup> were pre-

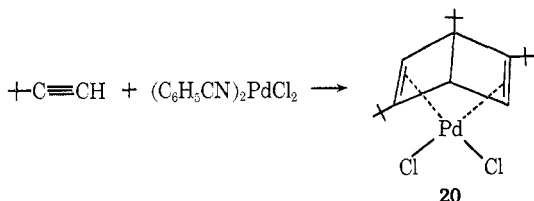


pared by utilization of benzyne cycloaddition reactions as principal synthetic devices.

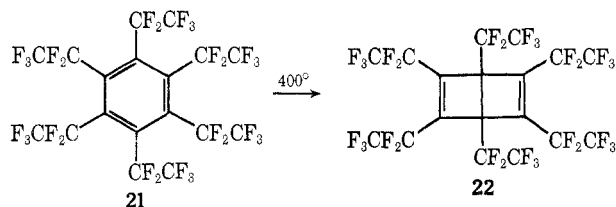
Newer methods for the synthesis of Dewar benzene systems have also emerged, including some dependent on metal-promoted reactions. Pettit<sup>20</sup> has utilized the ceric ion induced conversion of cyclobutadieneiron tricarbonyl (**18**) to cyclobutadiene as the starting point in



one approach, the transient hydrocarbon being allowed to react *in situ* with an acetylene, to give Dewar benzene product. Direct involvement of a metal in Dewar benzene formation is illustrated by the trimerization of *tert*-butylacetylene by bis(benzonitrile)palladium dichloride, a reaction which produces a palladium dichloride complex of 1,2,5-tri-*tert*-butyl(Dewar benzene) (**20**)<sup>21</sup> In a noteworthy extrapolation of the steric



strain approach, Haszeldine and coworkers have discovered that hexakis(pentafluoroethyl)benzene (**21**) is



quantitatively converted in a *thermal* reaction, carried out at 400° in a platinum flow system, to the Dewar benzene **22**.<sup>22</sup>

The field of photoinduced isomerization of polysubstituted benzenes has been treated incisively by Kaplan and Wilzbach. After observing this photoreaction in various simple systems,<sup>23</sup> these investigators proved

(17) H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, **90**, 1085 (1968).

(18) R. N. McDonald and D. G. Frickey, *ibid.*, **90**, 5315 (1968).

(19) D. T. Carty, *Tetrahedron Lett.*, 4753 (1969).

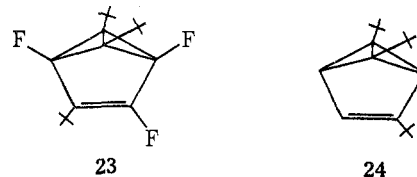
(20) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).

(21) M. Avram, E. Avram, G. D. Mateescu, I. G. Dinulescu, F. Chivaleu, and C. D. Nenitzescu, *Chem. Ber.*, **102**, 3996 (1969).

(22) E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, *Chem. Commun.*, 1216 (1969).

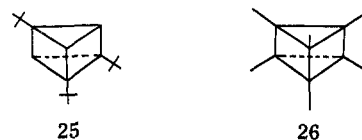
through the use of <sup>14</sup>C-labeled materials that ring isomerization does in fact occur.<sup>8</sup> Later studies showed that all three valence bond isomer levels are involved in the photointerconversions of representative benzenoid cases.<sup>24</sup>

Turning to the bicyclic series, we note that, *e.g.*, the trimerization which yields Dewar benzene **12** also generates concurrently the so-called "benzvalene" system (**23**)<sup>12</sup> Discussed by Hückel in 1937,<sup>25</sup> the

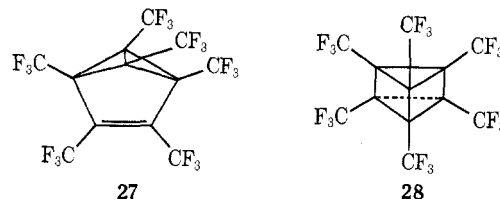


benzvalene structure was also considered in 1962 in connection with the photoisomerization of 1,2,4-*tert*-butylbenzene,<sup>1</sup> from which the isomer **24** does in fact derive.<sup>24</sup> Benzvalene itself can be isolated after ultraviolet irradiation of liquid benzene.<sup>17,26</sup>

Although the *tert*-butylfluoroacetylene trimerization was originally believed to produce a prismane ("Ladenburg benzene"),<sup>12</sup> the product was shown later to be actually a tetramer.<sup>27</sup> However, the irradiation of 1,2,4-tri-*tert*-butylbenzene does give rise to not only the mono and bicyclic isomers, but also the first recorded tricyclic example, the prismane **25**.<sup>24</sup> Criegee and



coworkers later synthesized a close relative of **25**,<sup>28</sup> while two groups effected the photoconversion of hexamethyl(Dewar benzene) to the simpler prismane **26**.<sup>29,30</sup> Photolysis of hexakis(trifluoromethyl)benzene produces not only the Dewar isomer **13** (as described above), but also the benzvalene **27** in major amount. A minor



component of the photolysis product is the prismane **28**, which is separately generated by irradiation of Dewar benzene **13**.<sup>15b</sup> The parent tricyclic benzene isomer case remains unknown.

Having in hand parent Dewar benzene, we carried out

(23) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **86**, 2307 (1964).

(24) K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965).

(25) E. Hückel, *Z. Elektrochem.*, **45**, 752, 760 (1937).

(26) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1031 (1967).

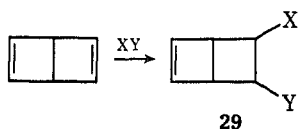
(27) H. G. Viehe, *Angew. Chem.*, **77**, 768 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 746 (1965).

(28) R. Criegee and R. Askani, *ibid.*, **5**, 519 (1966).

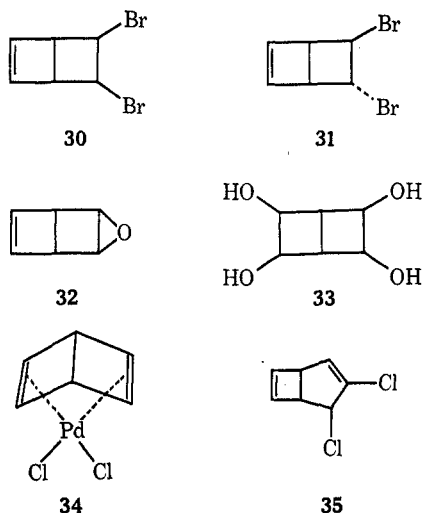
(29) D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966).

(30) W. Schäfer, R. Criegee, R. Askani, and H. Gruner, *Angew. Chem., Int. Ed. Engl.*, **6**, 78 (1967).

during the mid 1960's varied studies of its chemical behavior.<sup>31</sup> Most reactions were those anticipated for reactive  $\pi$  bonds in a small-ring framework, involving ready, uncomplicated formation of addition products (**29**) resulting from attack by various reagent types.

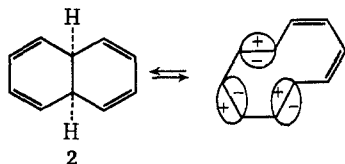


On treatment with molecular bromine, Dewar benzene is converted to a mixture of cis and trans bicyclic dibromides **30** and **31**, in addition to smaller amounts of



two tetrabromides. Similarly, peracid effects transformation to monoepoxide **32**, while osmium tetroxide oxidation gives rise to the tetrol **33**. A coordination compound (**34**) of unrearranged hydrocarbon is formed on reaction of Dewar benzene with bis(benzonitrile)-palladium dichloride. On the other hand, ring expansion occurs during addition of dichlorocarbene, giving the bicycloheptadiene **35**. In fact, in Dewar benzene reactions, aromatization was found the exception! Again, such behavior can be rationalized by application of the Woodward-Hoffmann rules in their simplest form:<sup>4,32</sup> the conrotatory, thermal conversion of cyclobutene would afford, in these cases, impossibly strained  $\pi$  bonds within the cyclic framework.

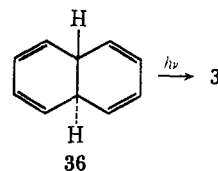
Interest in the 9,10-dihydronaphthalene system was based on its relationship to cyclodecapentaene and the possibility of converting the former to the latter, at the time an unknown  $(4n + 2)$ - $\pi$ -electron structure. Following the preparation of *cis*-9,10-dihydronaphthalene (**2**), the first monocyclic valence bond isomer of



(31) E. E. van Tamelen and D. Carty, *J. Amer. Chem. Soc.*, **89**, 3922 (1967).

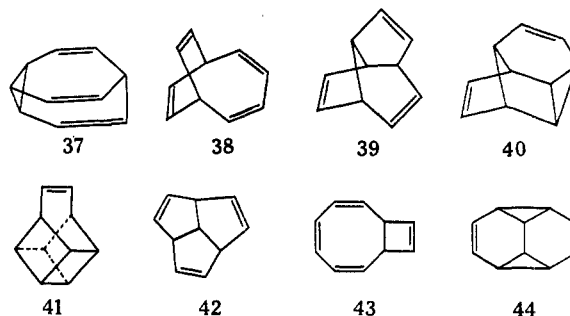
(32) For a similar study with hexamethyl(Dewar benzene), see W. Schäfer and H. Hellmann, *Angew. Chem., Int. Ed. Engl.*, **6**, 518 (1967).

cyclodecapentaene, attention was turned to the trans isomer, a potential precursor of a cyclodecapentaene by the more attractive photochemical route. Although permitted by the orbital symmetry rules,<sup>4</sup> the *cis* isomer was not transformed thermally to a cyclodecapentaene, thus signifying that the latter parent is a relatively unstable  $(4n + 2)$ - $\pi$ -electron case. In keeping with this expectation, the trans isomer **36** was



convertible by irradiation, in accordance with the Woodward-Hoffmann rules, to a new, highly unstable product, shown to be parent cyclodecapentaene (**3**).<sup>33</sup>

In the meantime, important new  $(CH)_{10}$  hydrocarbons were obtained in other laboratories, including bullvalene (**37**),<sup>34</sup> bicyclo[4.2.2]decatetraene (**38**),<sup>35</sup>



tricyclics **39** and **40**,<sup>36</sup> "basketene" (**41**),<sup>37</sup> and triquinacene (**42**).<sup>38</sup> More recently, bicyclo[6.2.0]decatetraene (**43**)<sup>39</sup> and the tetracycle **44**<sup>40</sup> have been isolated and identified. The theoretical and observed interrelationship of these valence bond isomers is a fascinating subject, and, as pointed out elsewhere,<sup>41</sup> *cis*-9,10-dihydronaphthalene has emerged as a low-energy reference species to which many isomers tend to convert, whether permitted or not by the Woodward-Hoffmann rules. Also, mention must be made in this whole connection of the accomplishments of Vogel, especially the synthesis and study of the first 1,6-bridged cyclodecapentaenes (**45**), aromatic valence bond isomers of the 9,10-dihydronaphthalene type **46**.<sup>42</sup>

(33) E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967); E. E. van Tamelen and R. H. Greeley, *Chem. Commun.*, 601 (1971).

(34) G. Schroder, *Chem. Ber.*, **97**, 3140 (1964).

(35) (a) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966); (b) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); (c) M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967).

(36) M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

(37) (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); (b) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); (c) R. Furstoff and J. M. Lehn, *Bull. Soc. Chim. Fr.*, 2497 (1966).

(38) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964).

(39) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89**, 4594 (1967).

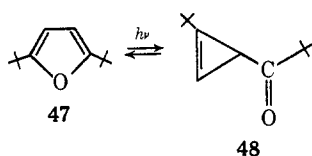
(40) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968).

(41) E. E. van Tamelen and B. C. T. Pappas, *ibid.*, **93**, 6111 (1971).

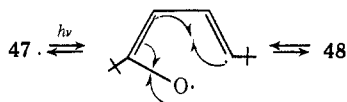
(42) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964).



Recognition of authentic valence bond isomers of benzene brought to mind the question of whether comparable isomers of aromatic heterocycles might be gotten in hand. Our own interest in this matter centered again on the preparation and isolation of stable valence bond isomers of traditional, simple aromatic systems bearing one heteroatom in the  $\pi$  framework. By means of experiments directly modeled after the photoformation of tri-*tert*-butyl(Dewar benzene) from tri-*tert*-butylbenzene,<sup>1</sup> the stable *tert*-butylcyclopropenyl *tert*-butyl ketone **48** was shown to form on photolysis of di-*tert*-butylfuran **47** and to revert to the latter on in-

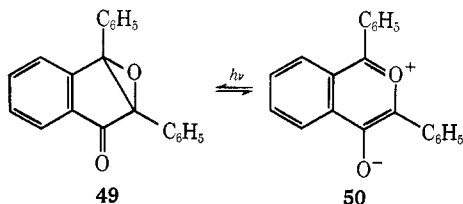


dependent irradiation.<sup>43</sup> Working with simpler furans, Srinivasan was able to isolate nonisomeric photo-products (*e.g.*, cyclopropenes), the formation of which was taken to indicate valence bond isomerization of the type **47**  $\rightarrow$  **48**.<sup>44</sup> Thus, with furans, there is observed



a new kind of "valence bond isomerization," one involving ring contraction of a type not observed thus far for aromatic hydrocarbons, and apparently involving a mechanism featuring formation and reclosure of an acyclic diradical.

Although involving more unusual heterocyclic components, the work of Ullman and coworkers resulted in the obtention of the first observed valence bond isomer of an aromatic heterocycle:<sup>45</sup> the indenone oxide **42** was shown to be interconvertible with the pyrylium oxide **50**. Similarly, the isoxazole **51** is transformed to azirine



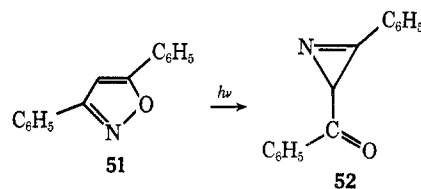
**52** under photolytic conditions.<sup>46</sup>

(43) E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968).

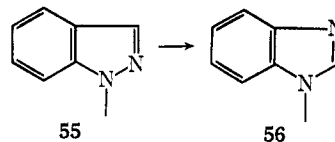
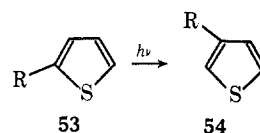
(44) R. Srinivasan, *ibid.*, **89**, 1758 (1967); **89**, 4812 (1967).

(45) E. F. Ullmann and J. E. Milks, *ibid.*, **84**, 1315 (1962).

(46) E. F. Ullmann and B. Singh, *ibid.*, **88**, 1844 (1966); **89**, 6911 (1967).

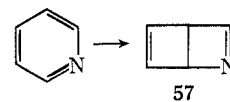


Finally, various photolytic conversions of a given substituted heterocycle to an isomer in the same heterocyclic category leave little doubt that valence bond isomerizations of aromatic systems are involved, processes superficially comparable to the ultraviolet-induced isomerization of polysubstituted benzenes. In this context, the work of Wynberg is prominent,<sup>47</sup> dealing principally with interconversion of thiophenes, *e.g.*, **53**  $\rightarrow$  **54**. Noteworthy investigations in this area

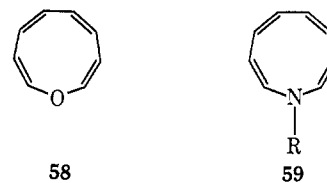


have also been published by Schmid and coworkers, who reported *inter alia* the conversion **55**  $\rightarrow$  **56**.<sup>48</sup> Elsewhere a detailed interpretation of the behavior of excited five-membered aromatic heterocycles is presented.<sup>49</sup>

Within the last year, evidence has been supplied to indicate that pyridine on photolysis generates the Dewar type isomer **57**.<sup>50</sup> Also, there have been re-



ported various valence bond isomers of the ten- $\pi$ -electron systems, oxacyclononatetraene (oxonin) (**58**)<sup>51</sup> and azacyclononatetraene (azonine) (**59**).<sup>52</sup> Irradiation of



(47) H. Wynberg and H. van Driel, *ibid.*, **87**, 3998 (1965).

(48) (a) H. Goth and H. Schmid, *Chimia*, **20**, 148 (1966); (b) H. Tiefenthaler, W. Dorscheln, H. Goth, and H. Schmid, *Tetrahedron Lett.*, 2999 (1964).

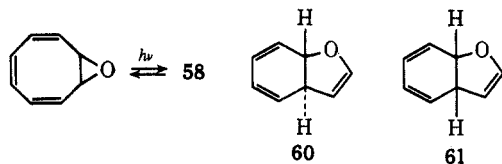
(49) E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **93**, 6129 (1971).

(50) K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, **92**, 2178 (1970).

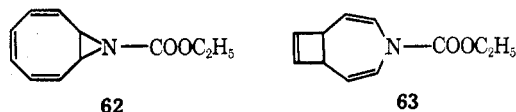
(51) (a) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 1521 (1969); (b) J. M. Holovka, R. R. Grabbe, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *ibid.*, 1522 (1969); (c) S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

(52) (a) A. G. Anastassiou and J. H. Gebrian, *ibid.*, **91**, 4011 (1969); (b) S. Masamune, K. Hojo, and S. Takeda, *Chem. Commun.*, 1204 (1969).

cyclooctatetraene oxide, a long-known valence bond isomer of **58**, provided **58**, which in turn acts as a precursor of the additional cases **60** and **61**. Along similar

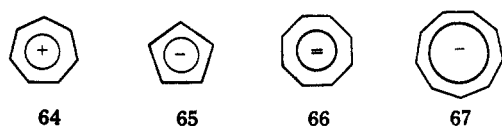


lines, the valence bond isomers of **59** ( $R = \text{COOC}_2\text{H}_5$ ), namely **62** and **63**, have been synthesized and shown to

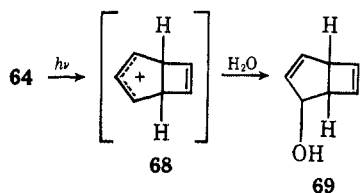


afford the azonine on irradiation.

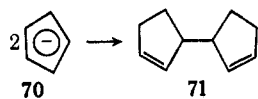
In searching for valence bond isomers of distinctly different aromatic entities, we focused attention on charged carbon types, including the well-known tropylium ion (**64**), cyclopentadienyl anion (**65**), cyclo-



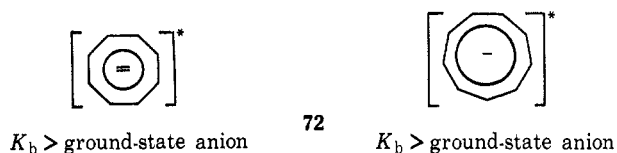
octatetraenyl dianion (**66**), and cyclononatetraenyl anion (**67**). Only in the tropylium ion case did valence bond isomerization occur: photolysis of the aromatic in an aqueous system provided the bicyclic alcohol **69**,



generated by solvolysis of the immediate irradiation product, "Dewar tropylium ion" (**68**).<sup>53</sup> With the other aromatics mentioned, different photochemical phenomena occurred, including: (1) reductive coupling (**70** → **71**)<sup>54</sup> and (2) conversion to excited state species



(**72**) possessing an order of basicity significantly higher



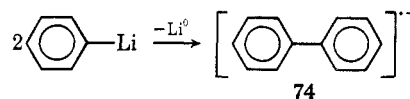
than that characteristic of the ground-state counterpart.<sup>55</sup> By photolytic means it was possible to generate

the hydrocarbon **73** corresponding to the valence bond

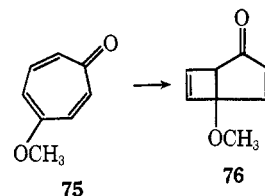


isomer of cyclopentadienide. However, as clearly demonstrated, the hydrocarbon arises by direct irradiation of cyclopentadiene, not the corresponding anion.<sup>56</sup>

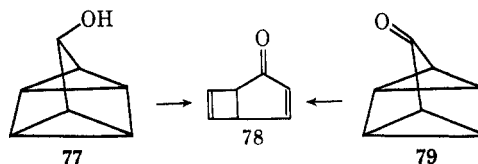
In a different connection, the behavior of excited phenyllithium was studied. Although this molecular type did not detectably isomerize to "Dewar phenyl anion" and thereby provide a convenient source of Dewar benzene, a new reaction did come to light: photocoupling with loss of lithium metal to the radical anion of biphenyl (**74**).<sup>57</sup>



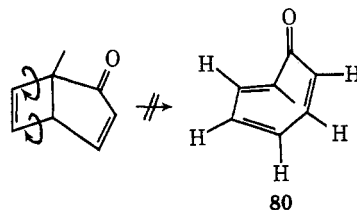
The photochemistry of tropolone and troponone derivatives<sup>58</sup> has also been pursued continuously starting with the isomerization of  $\gamma$ -tropolone methyl ether (**75**) to bicyclic ketone **76**. In 1965, the parent bicyclohepta-



dienone (**78**) was reported, arising either from **77** under Oppenauer oxidation conditions or from **79** by the



action of alumina. All of these substances—valence bond isomers of the  $(4n + 2)$ - $\pi$ -electron aromatic type, troponone—are remarkably stable, temperatures in the vicinity of  $350^\circ$  being used for conversion to the monocyclic parent. As in previous cases discussed herein, their stability is explicable by inhibition of the normally stereoelectronically preferred conversion to *trans*,*cis*-1,3-diene (**80**).



(53) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(54) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **89**, 5073 (1967).

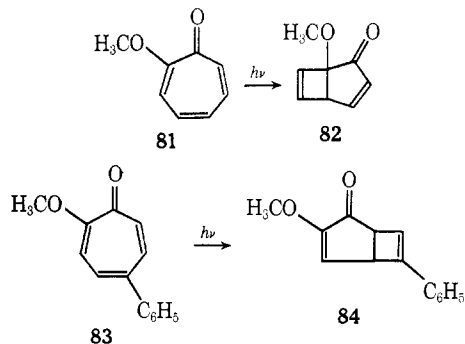
(55) J. I. Brauman, J. Schwartz, and E. E. van Tamelen, *ibid.*, **90**, 5328 (1968).

(56) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966).

(57) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **87**, 4964 (1965).

(58) For a summary of earlier work, see ref 3a.

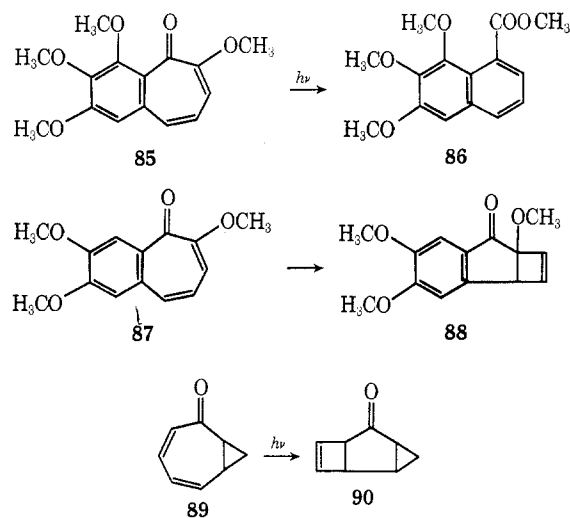
In more recent times, additional valence bond isomerizations in the tropone-tropolone series have come to light. While 2,5 bonding occurs in the photoisomerization of simple  $\alpha$ -tropolones (**81**  $\rightarrow$  **82**),



5-phenyltropolone methyl ether (**81**) permits 4,7-bonding in the ring-closure operation, leading to cyclopentenone **82**. Other 5- and 6-substituted (phenyl and chloro) tropolones and the corresponding ether gave rise on irradiation to mixtures of bicyclic products resulting from concurrent 2,5- and 4,7-bonding processes.<sup>59</sup> In the benzotropolone series, whereas tetra-*O*-methylpurpurogallin (**85**) suffers photochemical ring contraction, giving methyl 6,7,8-trimethoxynaphthoate

(59) T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967); T. Mukai and T. Shishido, *J. Org. Chem.*, **32**, 2744 (1967).

(**86**),<sup>60</sup> the demethoxy analog **87** provides instead photo-



product **88**.<sup>61</sup> In a distinctly different vein, the homo-tropone **89** has been observed to give, on photolysis, the tricyclic ketone **90**,<sup>62</sup> probably the first observed valence bond isomer of a homoaromatic system.

(60) E. J. Forbes and R. A. Ripley, *J. Chem., Soc.*, 2770 (1959); O. L. Chapman and T. J. Murphy, *J. Amer. Chem. Soc.*, **89**, 3476 (1967).

(61) E. J. Forbes and J. Griffiths, *J. Chem. Soc. C*, 2072 (1966).

(62) L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).