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A RATIONAL SYNTHESIS OF BULLVALENE[1] BARBARALONE AND DERIVATIVES; BULLVALONE

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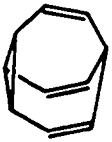
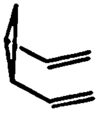
Abstract— A rational synthesis of bullvalene (I) proceeds in seven steps from cycloheptatriene-7-carboxylic acid by way of cycloheptatriene-7-carbonyl chloride, cycloheptatrien-7-yl diazomethyl ketone (B-1), barbaralone (VI), bullvalone (V), 9-hydroxytricyclo [$3.3.2.0^{2,8}$]deca-3,6-diene and 9-acetoxytricyclo-[$3.3.2.0^{2,8}$]deca-3,6-diene (F-4). Discussion is concerned mainly with (a) an attempt to synthesize bullvalone (V) from cycloheptatriene-7-ylacetic acid (A-1) which instead produced the isomeric tricyclo[$5.3.0.0^{2,10}$]-deca-3,5-dien-9-one (A-3); (b) the divinylcyclopropane rearrangement in barbaralone (V) and the theoretical relation of its very rapid rate to Cope rearrangement in acyclic systems; (c) the preparation and fluxional quality of barbaralane (VII); (d) the thermal reorganization of bullvalene (I) to *cis*-9,10-dihydronaphthalene (IX); (e) the preparation of methyl- and phenyl-bullvalene; and (f) the exchange of all ten hydrogen atoms in bullvalone (V) by deuterium and the bearing of this observation on the fluxionality of bullvalene (I).

Tricyclo[$3.3.2.0^{2,8}$]deca-3,6,9-triene (I, bullvalene) evolved conceptually[6] as the logical consequence of the successful demonstration that bicyclo [5.1.0]-octa-2,5-diene (II, homotropilidene)[7] possesses fluxional character owing to a rapid, structurally degenerate divinylcyclopropane rearrangement.


I

II


III


IV

In the generalized definition, a structurally fluxional molecule is characterized not by a single equilibrium arrangement of bonding atoms but by the existence of

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[1] Preliminary announcements of parts of this work are to be found in reviews by Doering and Roth[2] and by Schröder, Oth and Merényi [3]

[2] W. von E. Doering and W. R. Roth, *Angew. Chem.* **75**, 27 (1963); *Inter. Ed.* **2**, 115 (1963).

[3] G. Schröder, J. F. M. Oth and R. Merényi, *Angew. Chem.* **77**, 774 (1965); *Inter. Ed.* **4**, 752 (1965).

[4] We wish to express our deep gratitude to the Aaron E. Norman Fund for the awards of the Ruth Alice Norman Weil Postdoctoral Fellowship in Organic Chemistry to Dr. Barbara M. Ferrier (October 1961 September 1962), the Sylvan E. Weil Postdoctoral Fellowship in Organic Chemistry to Dr. M. Jones, Jr. (January–August 1963) and the Hickrill Chemical Research Foundation Postdoctoral Fellowship in Organic Chemistry to Dr. G. Klumpp (November 1962–May 1964).

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[6] W. von E. Doering, *Zh. Vsesoyuz. Khim. Obshchestva im D. I. Mendeleeva* **7**, 308 (1962).

[7] W. von E. Doering and W. R. Roth, *Tetrahedron* **19**, 715 (1963).

two or more identical chemical structures which are interconverted by an autogenous[8] intramolecular rearrangement at a rate high enough to demand acknowledgement for certain chemical purposes.[9]

The broad line of logical development to bullvalene (I) begins with hexa-1,5-diene (IV), which suffers a degenerate Cope[11] rearrangement rapidly at 300° and above.[12] The second stage proceeds to the *cis*-divinylcyclopropane (III)[7] of Vogel *et al.*,[13] the as yet unisolated[7] molecule which rearranges very rapidly owing to the relief of the strain in the cyclopropyl ring but has lost the potentiality for a degenerate rearrangement inherent in hexa-1,5-diene. The third stage of development progresses to homotropilidene, bicyclo[5.1.0]octa-2,5-diene (II),[7] in which the degeneracy lost in III is restored by the second methylene group (4) and the rapidity of the divinylcyclopropane rearrangement is retained despite the necessarily 6-center conformation of the transition state.[14] Finally, the addition of a third double bond as a bridge between C_4 and C_8 in II culminates the development by freezing the divinylcyclopropane structure in the kinetically preferred *syn* conformation. At the same time, the number of structures needed to describe the three-fold symmetrical bullvalene (I)[15] increases to 1,209,600 from the two needed to describe homotropilidene (II).

By the middle of 1963 in one characteristically spectacular stroke,[16] Gerhard Schröder had obtained bullvalene[17] by UV irradiation of the 76° dimer of cycloöctatetraene, which was simultaneously corrected from pentacyclo[8.4.2.0.^{2,9}0.^{3,8}0^{11,14}]hexadeca-4,6,12,15-tetraene, originally assigned by W. O. Jones,[18] to pentacyclo[9.3.2.0.^{2,14}0.^{3,10}0^{4,9}]hexadeca-5,7,13,15-tetraene.

The present paper concerns an alternate synthesis of bullvalene, which in its rationality offers independent synthetic evidence for the structure, and an investigation of

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[8] "Autogenous" in a chemical sense defines an aphotic, uncatalyzed (or self-catalyzed, self-generated) reaction.

[9] Although tautomerism[10] has long defined the behavior of systems of two or more readily interconvertible isomers, a word for the separate description of degenerate examples has not been available. The special property of a molecule which may suffer a degenerately tautomeric rearrangement is the ability to be rapidly rearranged into itself by a physical process (such as rotation in ethane or inversion in ammonia) or a chemical process (the breaking and remaking of bonds). Fluxion ("continuing motion or change") and fluxional seem eminently appropriate words to designate molecules which are able to undergo rapidly reversible, structurally degenerate isomerizations.

[10] J. W. Baker, *Tautomerism*. van Nostrand, New York (1934).

[11] H. Levy and A. C. Cope, *J. Am. Chem. Soc.* **66**, 1684 (1944).

[12] W. von E. Doering and V. Toscano have found that 1,1-dideuteriohexa-1,5-diene (IV) rearranges to 3,3-dideuteriohexa-1,5-diene at a convenient rate in the range of temperatures, 250–350°, with activation parameters, $E_a = 35{\cdot}5$ kcal/mole and $\Delta S^{\ddagger} = -9{\cdot}0$ e.u. [unpublished, but see footnote 9 in J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.* **86**, 5017 (1964)].

[13] E. Vogel, K.-H. Ott and K. Gajek, *Liebigs Ann.* **644**, 172 (1961).

[14] W. von E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962).

[15] The precise origin of this ignoble name, at the hands of incredulous graduate students, is lost, but their initial response to its conception and the possibility of its existence is suggested in E. Partridge, *A Dictionary of Slang and Unconventional English* p. 104. Macmillan, N.Y. (1961).

[16] G. Schröder, *Angew. Chem.* **75**, 772 (1963); *Inter. Ed.* **2**, 481 (1963).

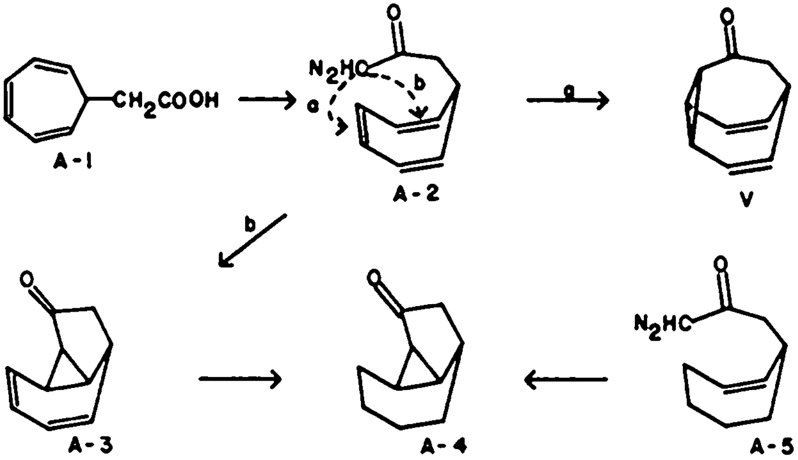
[17] The simplicity with which Schröder wrote on 18 May 1963 of these brilliant achievements bears sharing: "Die letzten Wochen und Monate habe ich mich weiterhin mit der Strukturbestimmung der fluktuierenden Moleküle $C_{16}H_{16}$ und $C_{12}H_{12}$ beschäftigt. Dabei ist mir *völlig ungewollt und unbeabsichtigt* Ihr 'Bullvalene' in die Hände gefallen."

[18] W. O. Jones, *Chem. & Ind.* 16 (1955).

bullvalone (V), which plays a vital role in the establishment of the fluxional character of the bullvalene system.

The first synthetic attempts started with the readily available cycloheptatrien-7-ylacetic acid (A-1)[19, 20] and proceeded to the diazoketone (A-2) with a view to effecting copper-catalyzed decomposition and cyclization.[21, 22] It was intended that ring closure should involve the transannular double bond (a) and lead to bullvalone (V), but, in fact, the divalent intermediate attacked an adjoining double bond (b) and led to an isomeric ketone, A-3.

Chart A



Independent evidence for the structure of A-3 includes its UV spectrum [λ_{max} 255 mμ, ε 4200], which is almost the same as that of a related diene, bicyclo[5.1.0]-hepta-2,4-diene[7] [λ_{max} 258 mμ, ε 4200]; the UV spectrum of the conjugate crystalline alcohol obtained from A-3 by reduction with sodium borohydride [λ_{max} 260 mμ, ε 4640], which is also characteristic of a conjugated diene; and the difference spectrum of equimolar solutions of the alcohol and A-3 [λ_{max} 293 mμ, ε 138], which clearly reveals the ketone function. Further evidence is provided by examination of the three products of catalytic hydrogenation one of which is tricyclo[5.2.1.0^{2,10}]-deca-9-one (A-4) which has been synthesized from A-5.[22] The other two products have retention times (GLPC) identical with the retention times of the two products of hydrogenation of A-4.

Other conditions for the decomposition of A-2, such as photochemical, thermal and catalytic (cuprous tetrachloraluminate), failed to divert the "ketocarbene" from the proximate double bond to the transannular bond. Examination of models of the *syn* conformation of 7-substituted cycloheptatrienes encouraged the belief that the lower homologous "ketocarbene" (from B-1) might find it more difficult

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[19] M. E. Volpin, I. S. Akhrem and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1501 (1957).

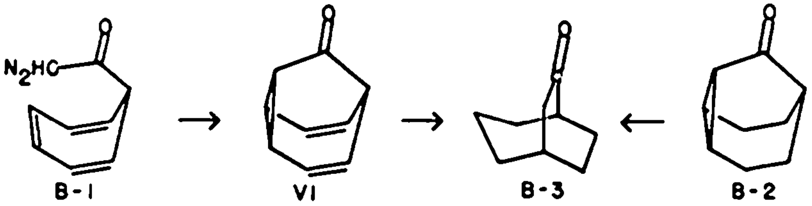
[20] K. Conrow, *J. Am. Chem. Soc.* **81**, 5461 (1959).

[21] G. Stork and J. Ficini, *J. Am. Chem. Soc.* **83**, 4678 (1961).

[22] W. von E. Doering, E. T. Fossel and R. L. Kaye, *Tetrahedron* **21**, 25 (1965).

to react with the proximate double bond. In fact, this prediction could be realized,[2, 3] but the resulting molecule VI was inevitably one carbon atom shy of the required ten.

Chart B

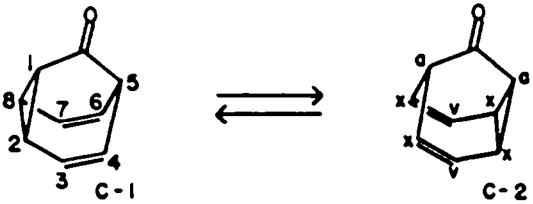


The sequence proceeds from benzene and ethyl diazoacetate[23, 24] through cycloheptatrien-7-ylcarbonyl chloride[24] to cycloheptatrien-7-yl diazomethyl ketone (B-1). Reaction with copper powder or cuprous ion produces tricyclo[3.3.1.$0^{2,8}$]-nona-3,6-dien-9-one (VI, barbaralone).

Independent chemical evidence to support the structure of barbaralone is derived from its catalytic hydrogenation to two ketones, one of which appears to be bicyclo-[3.2.2]nonan-6-one (B-3). This material is also the major ketone formed in the catalytic hydrogenation of tricyclo[3.3.1.$0^{2,8}$]nonan-9-one (B-2)[22] and must have either the structure B-3 or bicyclo[3.3.1]nonan-9-one. Since the former is expected to exchange deuterium in the presence of base and deuterium oxide, while the latter is not, the fact that the ketone exchanges deuterium supports the assignment of bicyclo[3.2.2]nonan-6-one (B-3).

The NMR spectrum imposes further stringent conditions on the structure of VI and reveals its fluxional character. This spectrum derives, at room temperature or above, from the average of two rapidly equilibrating, structurally indistinguishable valency tautomers (C-2) whereas the low-temperature spectrum, determined by Lambert,[25] corresponds to that of the single-structured, frozen molecule (C-1).

Chart C



Below -70°, the spectrum reveals four vinyl hydrogen atoms centered at $\delta = 5{\cdot}92$ ppm, three hydrogen atoms at $\delta = 2{\cdot}91$ ppm and one at 2·46 ppm. At higher temperatures, there appears a new band which, at room temperature or above, has become a sharply resolved component of the spectrum of the fluxional molecule. Centered at

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[23] W. von E. Doering and D. W. Wiley, *Tetrahedron* **10**, 183 (1960).

[24] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 2021 (1956).

[25] J. B. Lambert, *Tetrahedron Letters* 1901 (1963).

4·32 ppm and describable, oversimplified, as a triplet, this band of an area corresponding to four hydrogen atoms (type x) is the consequence of averaging two vinyl hydrogen atoms (4 and 6; 5·92 ppm) and two tertiary cyclopropane hydrogen atoms (2 and 8; 2·91 ppm). Two vinyl hydrogen atoms (3 and 7) remain at 5·71 ppm as type v, while two hydrogens α to the carbonyl group (type a) appear at 2·65 ppm as the average of the hydrogen atoms at the bridgehead (5; 2·91 ppm) and the tertiary cyclopropyl hydrogen (1; 2·46 ppm).

The fine structure of the room-temperature spectrum (C-2) lends further support to the assignment. Each of the two vinyl hydrogen atoms (type v) is split into a triplet by a pair of adjacent hydrogen atoms of type x, 2 and 4, and 6 and 8, respectively. Each arm of the triplet is itself split into a triplet by the pair of opposite hydrogen atoms of type x: atom 3 by 6 and 8; atom 7 by 2 and 4. Each hydrogen atom of type a becomes split into a triplet ($J = 7$ c/s) by the adjacent pair of type x: atom 1 by 2 and 8, atom 5 by 4 and 6. Finally, each of the four hydrogen atoms of type x is split by coupling with one hydrogen of type a and one of type v: e.g., atom 2 by 1 and 3. Owing to the fortunate near-identity of coupling constants, this coupling appears as a surprisingly clean triplet.

In earlier work on fluxional molecules,[7] it had been hypothesized that the *syn* conformation of bicyclo[5.1.0]octa-2,5-diene (homotropilidene, II) was kinetically more favorable to the divinylcyclopropane rearrangement than the *anti* conformation, which was suspected of being the thermodynamically more favorable conformation. On this reasoning an even more rapid rate of rearrangement was predicted of a molecule frozen permanently in the *syn* conformation by the incorporation of a bridge between atoms 4 and 8. In barbaralone (VI) such a molecule has been created and the rate of its divinylcyclopropane rearrangement is indeed much faster than that of II in accord with prediction.[26] The total amount of strain available for partial relief in the transition state may have increased sufficiently to contribute significantly to the increase in rate,[27] but the more precise allocation of the acceleration between enthalpy and entropy of activation will require the determination of several heats of formation, derivable energies of strain and presently unavailable rates.

Nevertheless, the remarkable rapidity of the divinylcyclopropane rearrangement in barbaralone deserves some comment at this time. The estimation of activation energies in this and related systems is based on the assumption of a transition state resembling a *bis*-allylic diradical (Chart D). The activation energy predicted for the rearrangement of *trans*-1,2-divinylcyclopropane (*trans*-III) is now estimated to be 30·5 kcal/mole on the basis of values somewhat different from those used previously.[7] The estimation is composed of the binding strength of two secondary carbon atoms (79 kcal/mole)[29] less the assistance of two elements of allylic energies of delocalization[30]

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[26] Although the rate of rearrangement of VIII has been determined by Lambert,[25] that of II is still undetermined. Roughly comparable degrees of averaging are found at −50° for VIII and 20° for II.

[27] That strain may be a significant factor in the acceleration is indicated by the very rapid rate of rearrangement found in semibullvalene.[28]

[28] H. E. Zimmermann and G. L. Grunewald, *J. Am. Chem. Soc.* **88**, 183 (1966).

[29] T. L. Cottrell, *The Strengths of Chemical Bonds* (2nd Edition) Butterworths, London (1958)

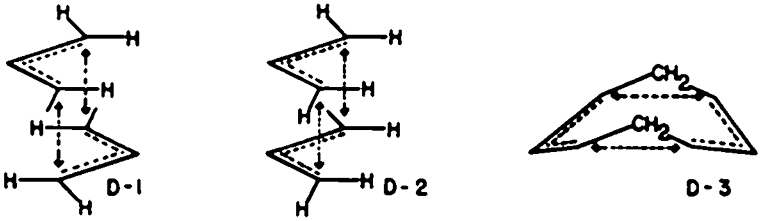
[30] Taken with reservations to be 17 kcal mole [half the difference between 81 kcal mole, the estimated binding strength of two primary carbon atoms, and 46·5 kcal mole, the activation energy of the formation of two allyl radicals from hexa-1,5-diene (W. von E. Doering and V. Toscano, unpublished)]. See J. B. Homer and F. P. Lossing, *Canad. J. Chem.* **44**, 2211 (1966)

(34·5 kcal/mole) less the assistance of strain to the opening of the cyclopropyl ring (16 kcal/mole)[31] plus two increments each of 1 kcal/mole assumed for the difference between *cis* and *trans* allylic radicals. This value of 30·5 kcal/mole agrees well with the value 32·1 kcal/mole recently reported by Vogel and Sundermann,[33] but it should be noted that changes of as little as ±2 kcal/mole in any of the contributing values could occasion a larger, but still acceptable, disparity between calculated and experimental values.

For the prediction of the activation energies of the divinylcyclopropane rearrangement in the tricyclic molecule, barbaralone (VI), in homotropilidene (II) in its *syn* conformation and in *cis*-1,2-divinylcyclopropane (III), assistance afforded by the cyclic or concerted nature of the reaction must be assessed. This element of concert is well recognized as the essential feature of the Cope rearrangement. Its geometrical requirement, elaborated recently in 3,4-dimethylhexa-1,5-diene,[14] involves a four-centered transition state ("acyclic" four-centered: 180°; D-1). The amount of assistance has been estimated to be 11 kcal/mole, the difference between the activation energies of the dissociation of hexa-1,5-diene to two allylic radicals[30] and the activation energy of the Cope rearrangement of 1,1-dideuteriohexa-1,5-diene.[12] Participation of a hypothetical 6-centered transition state ("acyclic" 6-centered: 0°; D-2) could not be detected and was thus estimated to be less effective than participation of the "acyclic" 4-centered state (D-1) by a minimum of 5-6 kcal/mole.

Unfortunately, this experience with an acyclic hexa-1,5-diene is of little help in the evaluation of possible assistance in the rearrangements of III, *syn*-II and VI. Owing to a fundamental difference in geometry, no arrangement even remotely resembling the "acyclic" four-centered transition state (D-1) is available when the two allylic radicals are connected through a carbon atom; that is, whenever atoms 3 and 4 of the hexa-1,5-diene are part of a small ring. In the Cope rearrangement of "acyclic" hexa-1,5-dienes, the two allylic radicals are in the *trans* relationship of the "acyclic" 4-centered state, whereas, in the related rearrangements of "cyclic" hexa-1,5-dienes (e.g. III, II and VI), they are obliged to be in a *cis* relationship, the strain-free form of which is the "cyclic" 4-centered (109°) transition state (D-3). It is thus unacceptable to assign an assistance of 11 kcal/mole or an activation energy of 21 kcal/mole (32 kcal/mole[33] minus 11 kcal/mole) to rearrangements of the *cis*-divinylcyclopropane type.

Chart D



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[31] The difference between 81 kcal/mole and the activation energy for *cis-trans* interconversion in cyclopropane (65·1 kcal/mole).[32]

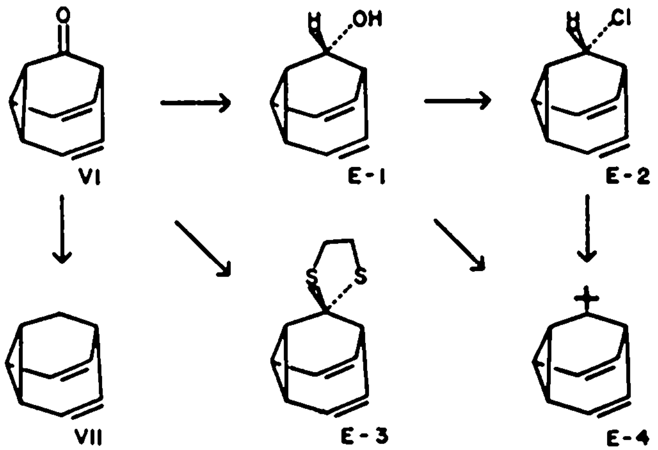
[32] E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.* **82**, 5996 (1960).

[33] E. Vogel and R. Sundermann, *Dissertation* Köln, 1966; graciously communicated privately by Professor Vogel with permission to cite.

It does not follow, however, that assistance from *cis*-overlap can be excluded on the grounds that this geometry is in essence a relative of the unobserved and unfavored "acyclic" 6-centered (0°) transition state (D-2). Alteration of this state to permit accommodation of the 3,4-bonding atom requires expansion of the dihedral angle of 0° to 109° ("cyclic" 4-centered: 109°; D-3). This expansion effectively reduces the repulsion of the filled non-bonding orbitals at atoms 2 and 5 of the allylic radicals by moving them too far apart for appreciable interaction. With this change in geometry the fundamental energetic objection to the 6-centered state is removed. Although a similar expansion is in principle available to the Cope rearrangement of "acyclic" hexa-1,5-dienes, it can not be employed profitably, owing to the presence of four interfering hydrogen atoms. These atoms effectively force the positively overlapping pairs of atoms 1 and 6 and 3 and 4 to separate almost as much as the negatively overlapping atoms 2 and 5. In summary, it is not clear theoretically whether side-by-side overlap in the "cyclic" 4-centered state (D-3) should be larger or smaller than the end-to-end overlap available in the "acyclic" 4-centered (180°) state (D-1). The experimentally observed assistance (*vide infra*) amounts to 20–24 kcal mole.

To determine whether the nature of the 9-substituent in the barbaralane system (Chart E) is a major factor influencing the high rate of rearrangement of barbaralone (VI), several derivatives have been made—the 9-hydroxyl (E-1), the 9-chloro (E-2), the ethylenedithioketal (E-3) and the parent hydrocarbon, barbaralane (VII).[34]

Chart E



All these substances undergo the divinylcyclopropane rearrangement at comparable rates in the sense that they possess averaged spectra at 25° and the spectra of single, frozen structures by −100°. Although a careful quantitative comparison is in progress, it is already clear that the presence of a carbonyl group at C_9 in VI exercises no great effect; in fact VI may react somewhat more slowly than the methylene analogue, barbaralane (VII).

Parenthetically, attempts have been made to scrutinize the C_9 carbonium ion

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[34] Barbaralane (VII) has just been synthesized by an alternate route through the tosylhydrazone of triasteranone [U. Biethan, H. Klusacek and H. Musso, *Angew. Chem.* **79**, 152 (1967); *Inter. Ed.* **6**, 176 (1967)].

(E-4) derivable from E-1 or E-2 for signs of anchimeric assistance and fluxional character. Not only have all efforts to observe the carbonium ion been fruitless,[35, 36] but even the tosylate derived from E-1 shows unexceptional reactivity.

The next step in the synthesis of bullvalene (I) requires enlargement of the ring in barbaralone (VI) by one carbon atom. This change, which is effected classically by diazomethane, leads to the desired ketone, bullvalone (V), and an aldehyde F-1 in about equal amounts. Since the IR spectrum of the crude product shows no aldehyde function, the aldehyde F-1 must be an artifact of the process of separation and purification by gas–liquid partition-chromatography and the result of an unexceptional acid-catalyzed rearrangement of the expected epoxide in the injection block or the column. An attempt to increase the yield of bullvalone by allowing diazomethane to react with the condensation product of VI and malononitrile was based on the work of Bastús,[37] but led to no improvement.

Independent evidence for the structure of bullvalone (V) is provided by its reduction to a saturated hydrocarbon, m.p. 167·5°, which has an IR spectrum identical with that of a saturated hydrocarbon, m.p. 179–180°, obtained by reduction of tricyclo-[3.3.2.0^{2,8}]decan-3-one (F-3).[22] Both reductions are effected by catalytic hydrogenation followed by application of the Huang Minlon modification of the Wolff-Kishner reduction. On the assumption that the structure of F-3 is unequivocally fixed by its method of synthesis from 4-cyclohepten-1-yldiazomethylketone (F-2),[22] the resulting saturated hydrocarbon must have the structure, bicyclo[3.3.2]-decane (VIII). Alder, Hartung and Hausmann claim to have synthesized a hydrocarbon of this structure, m.p. 162°, but the method of synthesis from cycloheptadiene and acrylonitrile involves a Demyanoff rearrangement and is therefore structurally open to question.[38] By the catalytic hydrogenation of bullvalene, Schröder obtained a hydrocarbon of m.p. 180°, for which the structure VIII was also claimed[39] but, at that time, bullvalene, standing in need of a proof of structure itself, could ill serve as the basis for the proof of structure of other molecules. The identity of Schröder's hydrocarbon and that obtained from F-3 has now been established.

Bullvalone shows carbonyl absorption at 1684 cm^{-1}. Its NMR spectrum is temperature-dependent and is outlined in the experimental section. Although full interpretation requires more experimental data, the thermodynamic equilibrium established by divinylcyclopropane rearrangement favors one of the two tautomeric forms to a significant degree. The shift in absorption in the vinyl region of the high-temperature spectrum is 20 c/s, from ca. 360 c/s to ca. 340 c/s, instead of 100 c/s to be expected if the two tautomers were of equal free energy. The ratio of the two isomers may thus be 9:1 or thereabouts. Consistent with its structure as a methylene ketone, bullvalone exchanges two atoms of deuterium quite rapidly at room temperature in dilute alkaline deuterium oxide.

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[35] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre and I. J. Bastien, *J. Am. Chem. Soc.* **86**, 1360 (1964).

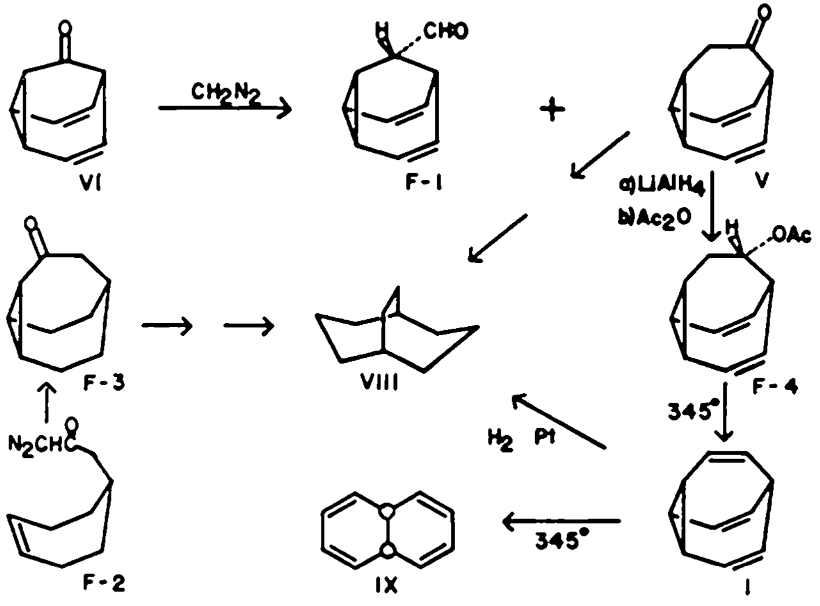
[36] T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.* **86**, 1600 (1964).

[37] J. B. Bastús, *Tetrahedron Letters* 955 (1963). See also F. Wessely, G. Adametz, A. Eitel and D. Swoboda, *Angew. Chem.* **76**, 107 (1964); *Inter. Ed.* **3**, 240 (1964).

[38] K. Alder, S. Hartung and G. Hausmann, *Chem. Ber.* **89**, 1972 (1956).

[39] G. Schröder, *Chem. Ber.* **97**, 3140 (1964).

Chart F



The conversion of bullvalone to bullvalene is effected by reduction with LAH to the corresponding carbinol and removal of elements of water. The carbinol, like bullvalone, is presumed to be an equilibrium mixture of the two divinylcyclopropane tautomers. It is converted by acetic anhydride in pyridine into a liquid acetate F-4, which is pyrolyzed in a flowing system at 345° to bullvalene (I) and *cis*-9,10-dihydronaphthalene (IX). Bullvalene is identified by direct comparison of a sample prepared according to the method of Schröder.[16, 39] Confirmation of its structure is obtained by unequivocal identification of one of the products of its catalytic hydrogenation with independently synthesized bicyclo[3.3.2]-decane (*vide supra*). *cis*-9,10-Dihydronaphthalene is identified by comparison of its NMR and UV spectra with those reported by van Tamelen and Pappas[40] in their original synthesis. Attempted catalytic reduction gives the disproportionation products, naphthalene and 1,2,3,4-tetrahydronaphthalene.

Closer investigation of the pyrolysis reveals that *cis*-9,10-dihydronaphthalene (IX) is the first product of the thermal reorganization of bullvalene and that the other products, including the naphthalene reported by Schröder,[39] are actually the products of the thermal reorganization of *cis*-9,10-dihydronaphthalene.[41] Coupled with the ready availability of bullvalene by Schröder's method this new formation constitutes a significantly improved method for the preparation of *cis*-9,10-dihydronaphthalene.

Schröder has already reported the most dramatic property predicted[6] of bullvalene: the merging of its low-temperature NMR spectrum into a single sharp absorption at higher temperature.[16] Shortly thereafter, Saunders determined the specific rate

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[40] E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.* **85**, 3296 (1963)

[41] W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.* **88**, 2078 (1966)

constant for the causative divinylcyclopropane rearrangement from NMR data and derived an activation energy, $E_a = 11{\cdot}6 \pm 1$ kcal/mole, for the process.[42]

His calculation was based on the Kubo treatment of NMR line shapes and accounted specifically for the four chemically distinct types of hydrogen. Subsequently, Schröder and his associates reported an activation energy of 13·1 kcal/mole[43] based on the simplifying assumption of a two-site model which permitted the use of the equation of Gutowsky and Holm.[44, 45] More recently, they reported without elaboration application of the method of Saunders.[3, 42] Last year, Allerhand and Gutowsky obtained the activation energy, $E_a = 12{\cdot}8 \pm 0{\cdot}1$ kcal/mole, by a study over a wide temperature range using the spin-echo magnetic resonance technique.[46]

Qualitatively the divinylcyclopropane rearrangement within bullvalene (I) proceeds at a considerably slower rate [$k = 3440$ sec^{-1} at 25° (extrapolated); $E_a = 11{\cdot}6$ kcal/mole[42]] than it does in barbaralone (VI) [$k = 193{,}000$ sec^{-1} at 25° (extrapolated); $E_a = 8{\cdot}1$ kcal/mole[25]] or in barbaralane (VII) [$k = 17{,}300{,}000$ sec^{-1} at 25° (extrapolated); $E_a = 8{\cdot}6$ kcal/mole (this work)]. Quantitative comparison is unjustified because the rate constants and activation energy for barbaralone were obtained by an inadequate treatment of the data. An internally consistent determination of the rates of rearrangement in a number of these systems is underway for the purpose of providing a quantitatively sound basis of comparison. However, it appears that the class of tricyclononadienes is generally more reactive than the class of tricyclodecadienes by some two to four powers of ten or 3-4 kcal/mole in the activation energy. Extra strain and its release in the transition state is a credible explanation of the acceleration in the smaller, tricyclononadiene system. No obvious electronic effect is discernible.

The synthesis of bullvalene by way of bullvalone is suitable for the synthesis of certain monosubstituted derivatives, such as methyl and phenylbullvalene reported here. The cycloöctatetraene method is in principle applicable to the synthesis of substituted bullvalenes but has not been turned to that purpose as yet. A fruitful method has been developed by Schröder from his observation that bromination of bullvalene leads to a dibromo derivative of bicyclo[3.3.2]decatriene from which bromobullvalene is easily obtained by elimination of hydrogen bromide.[43, 44] Bromobullvalene in turn has an easily displaceable bromide from which such derivatives as methoxy, ethoxy, and t-butyloxy bullvalenes[44] have been obtained. Since the presence of these substituents does not interfere with the bullvalene rearrangement, the remaining nine hydrogen atoms appear as a single NMR band at higher temperatures. Schröder has obtained phenylbullvalene by a delightful transformation of the 76° dimer of cycloöctatetraene with phenyllithium or other strong base to 8-phenyl-bicyclo[3.3.2]deca-2,6,9-triene followed by bromination and elimination of hydrogen bromide.[47]

In our syntheses, bullvalone is treated with methyl magnesium iodide or phenyllithium to give the corresponding tertiary alcohols from which water is easily elimi-

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[42] M. Saunders, *Tetrahedron Letters* 1699 (1963)

[43] G. Schröder, R. Merényi and J. F. M. Oth, *Tetrahedron Letters* 773 (1964).

[44] J. F. M. Oth, R. Merényi, J. Nielsen and G. Schröder, *Chem. Ber.* **98**, 3385 (1965).

[45] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 1228 (1956).

[46] A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.* **87**, 4092 (1965).

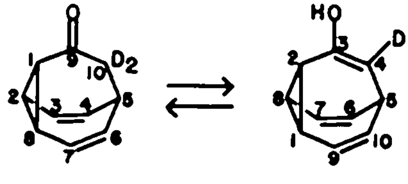
[47] G. Schröder, *Angew. Chem.* **77**, 682 (1965); *Inter. Ed.* **4**, 695 (1965).

nated to form methylbullvalene and phenylbullvalene, respectively. The striking characteristic of these materials is the NMR spectrum which at higher temperature shows the bullvalene ring system with a single type of hydrogen of relative area 9. Owing to the conjugative interaction of phenyl with a double bond, two reactions might have been detectable: the simple divinylcyclopropane rearrangement during which the phenyl remains conjugated and the slower bullvalene rearrangement during which the phenyl group must become bonded transiently to an unconjugated position. The conjugative interaction of a Ph group with a double bond (ca. 5·0 kcal/mole) might have provided a barrier of sufficient size to permit the separate observation of these two reactions, but it has not as yet been possible to separate them. The position of the methyl group at $\delta = 1{\cdot}75$ ppm in the low temperature spectrum is the same as at high temperature and suggests that the position of equilibrium among the four possible isomers is not observably sensitive to temperature. From its absolute chemical shift, the Me group appears to be allylic in type. Preference for this location is consistent with the high conjugative interaction of methyl (2·3 kcal/mole) with a double bond.

The potential usefulness of the bullvalene ring system in the evaluation of qualitative conjugative interactions is a useful consequence of its fluxional character. As an impressive illustration of this potentiality, Schröder has observed that fluorine is preferentially bonded to an aliphatic carbon atom whereas chlorine and bromine are preferentially bonded to olefinic carbon.[48]

The structural consequence of the fluxional character of bullvalene would be most clearly demonstrated in classical fashion by the finding that the unequivocal synthesis of a particular disubstituted derivative had in fact led to the equilibrium mixture of all the possible isomers. In the absence of such a demonstration, the temperature dependence of the NMR spectrum provides convincing evidence. Further evidence of a more nearly classical type is furnished by the base-catalyzed deuterium exchange of bullvalone.

Two of the hydrogen atoms of bullvalone exchange rapidly in dilute alkaline deuterium oxide in full accord with the presence of a methylene group α to the carbonyl group. If the experiment is continued while the extent of exchange is monitored by mass spectral analysis, further exchange is observed. Three, four and, finally, all ten hydrogen atoms are replaced by deuterium. This unique behaviour is clearly associated with the fluxional quality predicted of bullvalene.[6,7] By successive divinylcyclopropane rearrangements, each of the 1,209,600 arrangements of the ten methyne groups in bullvalene can be converted into the others and the ten carbon atoms appear to be distributed randomly. Bullvalone, which is not capable of undergoing the bullvalene rearrangement, is expected to be in equilibrium with a small amount of



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[48] G. Schröder, privately communicated with permission to cite.

its enolic tautomer, hydroxybullvalene, which is hypothetically capable of the bullvalene rearrangement. Thus the unexceptional product of exchange, the α,α-dideuterated bullvalone, 10,10-dideuteriotricyclo[3.3.2.0^{2,8}]-deca-3,6-dien-9-one, must be in equilibrium with its potentially fluxional relative, 4-deuteriotricyclo-[3.3.2.0^{2,8}]deca-3,6,9-trien-3-ol. Provided the conjugative interaction of the OH group with the double bond and the unfavorable equilibrium constant of the enolization do not conspire too effectively, the bullvalene rearrangement may now transport the deuterium from location 4 to some other part of the molecule and replace it by hydrogen which, having assumed a position α to the potential carbonyl group, will itself suffer exchange. In this manner ultimately all ten hydrogen atoms will be exchanged. Complete deuterium exchange provides strong evidence of a structural nature that the bullvalene rearrangement leads to random distribution of carbon atoms.

EXPERIMENTAL[49]

Tricyclo[5.3.0.0^{2,10}]*deca-3,5-dien-9-one* (**A-3**)

(a) *Cycloheptatriene-7-yl-acetyl chloride.* A mixture of 18·2 g cycloheptatriene-7-yl-acetic acid (**A-1**[19, 20] and 25 ml $SOCl_2$ was heated in 200 ml refluxing benzene for 1·5 hr. Removal of excess benzene and $SOCl_2$ by distillation on a steam-bath afforded crude acid chloride which was distilled *in vacuo* to give 15·3 g (76%), b.p. 65–69°/0·1 mm.

(b) *Cycloheptatrien-7-ylmethyl diazomethyl ketone* (**A-2**). The addition with stirring of a soln of 3 g acid chloride in 25 ml ether to a soln of diazomethane (prepared from 10 g N-nitroso-N-methylurea) in 100 ml ether at 0° was accompanied by vigorous evolution of gas. After 12 hr standing open at room temp, the mixture left an oily residue which was redissolved in ether, treated with charcoal, dried over $MgSO_4$ and concentrated. The residue was crystallized from pentane in long, yellow needles, m.p. 46·5–47°. (Found: C, 68·8; H, 5·6; N, 16·3. $C_{10}H_{10}N_2O$ requires: C, 68·9; H, 5·8; N, 16·1%.)

(c) *Copper-catalyzed decomposition of* **A-2** *to* **A-3**. Crude diazoketone from 6 g acid chloride was treated in 300 ml refluxing THF with 4 g Cu powder added in small portions over 1 hr. The mixture was refluxed for another hr, filtered and concentrated under reduced press. The oily residue was dissolved in ether, dried over $MgSO_4$, concentrated and evaporatively distilled to give 1·9 g of liquid ketone **A-3**; λ_{max} 255 mμ (ε = 4200).

Reduction of **A-3** (0·8 g) with KOH (0·8 g) and hydrazine hydrate (0·8 g) in diethylene glycol (8 ml) at 140° for 3 hr afforded an intensely blue hydrocarbon layer consisting mainly of azulene.

An oxime, prepared in the usual manner, could be crystallized from aqueous EtOH: m.p. 147° with dec. (Found: C, 74·7; H, 7·1. $C_{10}H_{11}NO$ requires: C, 74·5; H, 6·8%.) The UV spectrum in EtOH showed λ_{max} 220 mμ (ε = 3680) and 265 mμ (ε = 6650).

(d) *Tricyclo*[5.3.0.0^{2,10}]*deca-3,5-dien-9-ol.* A soln of 0·15 g $NaBH_4$ in 5 ml MeOH was added to a stirred soln of 0·56 g of **A-3** in 15 ml MeOH. After standing 3·5 hr at 25°, the mixture was concentrated to 10 ml by distillation *in vacuo* and treated with 10% $NaHCO_3$aq (10 ml). Three 15 ml ether extracts were dried over $MgSO_4$ and evaporated to 0·9 g colorless oil. Fractional crystallization from pentane gave 0·46 colorless prisms of the alcohol, m.p. 59–61°; λ_{max} 260 mμ (ε = 4640). (Found: C, 81·0; H, 8·3. $C_{10}H_{12}O$ requires: C, 81·1; H, 8·1%.)

The corresponding acetate was obtained as a low melting solid by boiling the alcohol for 5 min in a mixture of pyridine and Ac_2O. When this acetate was passed through a tube filled with alumina and heated to 400°, a brown oil was obtained which turned blue on exposure to air and then showed the characteristic UV spectrum of azulene.

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[49] NMR spectra are obtained with Varian Associates A-60 and HR-60 nuclear resonance magnetic spectrometers. We wish to acknowledge the assistance of Grant 22689 of the U.S. National Science Foundation in the purchase of the A-60 spectrometer. UV spectra are measured with a Cary Model 11S recording ultraviolet spectrometer. IR spectra are obtained with a Perkin-Elmer Model 421 grating infrared spectrometer.

(e) *Hydrogenation of tricyclo*[$5.3.0.0^{2,10}$]*deca-3,5-dien-9-one* (A-3). A soln of 0·08 g of pure A-3 in 5 ml EtOH was hydrogenated with 0·01 g 10% Pd–$CaCO_3$. The hydrogenation stopped after somewhat more than two equivs of H_2 had been asborbed. The soln was filtered, diluted with 8 ml n-hexane and concentrated by distillation of the EtOH hexane azeotrope through a 20-cm column packed with a nichrome coil. Gas chromatrographic analysis on a 5-ft, ¼ in. column of 33% Carbowax 20M on kieselguhr at 120° and 20 lb He revealed three components: A, ret. time of 1·0 min (rel. area 33); B, 2·8 min (1); C, 4·3 min (62). This third peak had the same retention time and the same IR spectrum as authentic tricyclo[$5.3.0.0^{2,10}$]-deca-9-one (A-4).[22]

When 0·4 g of A-4 was hydrogenated in 40 ml EtOH with 0·090 g 10% Pd $CaCO_3$ and the reaction mixture was treated with 50 ml n-hexane and concentrated by distillation of the azeotrope, a mixture of products was obtained. Analysis by GLPC revealed two products of retention times 1·0 min (5·2) and 2·8 min (1·0) in addition to recovered starting material. These two products are presumed identical with products A and B from the hydrogenation of A-3.

Tricyclo[$3.3.1.0^{2,8}$]*nona-3,6-dien-9-one* (VI, *barbaralone*)

(a) *Cycloheptatrien-7-carbonyl chloride*. This substance was prepared according to the sequence of reactions described by Dewar and Pettit.[24] Attempts to replace the *photochemical* generation of ethyl cycloheptatrien-7-yl-carboxylate[23] by the *thermal* reaction of ethyl diazoacetate in benzene according to Grundmann and Ottmann[50] were not successful. In the temp range 120–126° the reaction is very slow, while even in the range 130–139° considerable quantities of β and γ isomers are formed. Pure cycloheptatriene-7-carboxylic acid can be obtained but only by purification over the amide.

(b) *Cycloheptatrien-7-yl diazomethyl ketone* (B-1). To a stirred ethereal soln of diazomethane (prepared at 0° from 42 g N-methyl-N-nitroso-urea, 160 ml 50% KOHaq and 650 ml ether, dried over KOH pellets and distilled), there was added, dropwise, 14 g acid chloride (b.p. 79–80°/1 mm; n_D^{23} 1·5420) in 60 ml anhydrous ether over a period of 45 min at 0°. The mixture was allowed to stand at 4° for 12 hr, filtered and concentrated under reduced press without heat to give the diazoketone B-1 as a yellow oil.

(c) *Copper-catalyzed decomposition of* B-1 to VI. Without further purification, the diazoketone B-1 was dissolved in 80 ml anhyd benzene and 80 ml dry hexane and divided into two equal parts. The solns were each added dropwise to a vigorously stirred, boiling suspension of 16 g anhyd $CuSO_4$ in 160 ml n-hexane under N_2 over a 45 min period and refluxed for an additional hr. The supernatant liquid was decanted from the residue which was washed with acetone. The solns were combined, concentrated by distillation through a Vigreux column to about 80 ml, and subjected to steam distillation. The distillate was extracted with three 100-ml portions of ether. The ethereal extracts were dried over $MgSO_4$, concentrated to a volume of about 50 ml and cooled at −70°. The crystals were filtered by suction in a fritted glass funnel cooled to −70°. Recrystallization from 30 ml n-pentane once at −70° and again at −10 to −20° followed by vacuum sublimation gave 1·6 to 3·5 g, m.p. 40–48°. One crystallization from water afforded colorless needles, m.p. 53·5°. In the end-absorption of the UV spectrum, there are two shoulders at 225 mμ ($\varepsilon = 2710$) and 243 ($\varepsilon = 1840$). Carbonyl absorption in the IR is at 1700 cm^{-1}.

The NMR spectrum in CS_2 at 25° shows a triplet of relative area 2 centered at $\delta = 5·69$ ppm ($J = 7·3$ c/s) with each arm being further split into a triplet ($J = 1·5$ c/s); a triplet (complicated) of relative area 4 centered at $\delta = 4·20$ ppm ($J = 7·0$ c/s); and a triplet of relative area 2 centered at $\delta = 2·60$ ppm ($J = 6·5$ c/s).

An *oxime* was prepared by heating an aqueous ethanolic soln of hydroxylamine hydrochloride and AcONa on the steam bath for 10 min: colorless plates from aqueous EtOH, m.p. 130–131°. (Found: C, 73·5; H, 6·4; N, 9·5. C_9H_9NO requires: C, 73·5; H, 6·2; N, 9·5%.)

A *thiosemicarbazone* prepared in the usual manner was crystallized as prisms from EtOH: m.p. 165°. (Found: C, 59·0; H, 5·6; N, 19·7; S, 14·7. $C_{10}H_{11}N_3S$ requires: C, 58·5; H, 5·4; N, 20·5; S, 15·6%.)

A *semicarbazone* was obtained as precipitated crystals, m.p. 205–207° (dec), when a soln of 1·497 g VI, 1·5 g semicarbazide hydrochloride and 1·23 g AcONa in 8 ml water and 3 ml MeOH was allowed to stand overnight, yield: 2·130 g (99%).

The *p-toluenesulfonylhydrazone* was obtained by heating a soln of 150 mg VI and 300 mg *p*-toluenesulfonylhydrazine in 4 ml MeOH for 3·5 hr at 80°, adding a few drops of water and inducing crystallization by scratching with a glass rod: 245 mg (72%); m.p. 175–185° (dec); recrystallization from *p*-dioxan.

The *ethylene dithioketal* (E-3) was prepared by allowing a mixture of 300 mg VI in 2 ml ethanedithiol and 0·5 ml BF_3 Et_2O complex to stand at 0° for 12 hr. The colorless ppt was filtered and recrystallized

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[50] Ch. Grundmann and G. Ottmann, *Liebigs Ann.* **582**, 163 (1953).

from MeOH; 85 mg; m.p. 117–121°. The NMR spectrum is similar to that of VI: three triplets at δ = 5·66, 4·20 and 2·64 ppm and a singlet at 3·18 ppm of relative areas 1:2:1:2, respectively.

The malononitrile adduct is prepared by fusion of a mixture of 0·223 g VI and 0·12 g malononitrile. On addition of 5 mg pyridine the mixture warmed spontaneously and deposited crystals on standing. Recrystallization from Et_2O–AcOEt afforded 173 mg (60%) of condensation product, m.p. 145° after sublimation.

(d) *Hydrogenation of tricyclo*[3.3.1.$0^{2,8}$]*nona-3,6-dien-9-one* (VI). (1) A soln of 150 mg VI in 15 ml THF containing 50 mg 10% Pd–C was shaken with H_2 until no further reaction occurred: 104 ml H_2 was absorbed; theor. for 4 equiv., 102 ml. Filtration, concentration and recrystallization from pentane afforded colorless prisms of (presumably) bicyclo[3.3.1]nonan-9-ol: 0·127 g; m.p. 207° in a sealed tube. (Found: C, 77·2; H, 11·6; mol wt 140; $C_9H_{16}O$ requires: C, 77·0; H, 11·5%; mol wt 140.)

(2) When 58 mg VI was hydrogenated in EtOH or MeOH soln over 1% Pd–C until 3 equiv of H_2 had been absorbed, gas chromatographic analysis on a 2-m column of Carbowax 20M (20%) on kieselguhr at 120° and 10 lb He showed three components in about equal quantity: A, rel ret time 1·00; B, 1·16; and C, 3·21.

C has the same IR spectrum as the carbinol obtained in (1) above.

A is a ketone (IR 1730 cm^{-1}), from which a semicarbazone, m.p. 206–209° (dec) from aqueous EtOH, is obtained in the usual manner. Its IR spectrum is not identical with that of tricyclo[3.3.1.$0^{2,8}$]nonan-9-one (**B-2**).[22]

Ketone B (IR 1715 cm^{-1}) affords a semicarbazone, m.p. 199–201° (dec) from aqueous EtOH and has an IR spectrum identical with that of the major product of hydrogenation of tricyclo[3.3.1.$0^{2,8}$]nonan-9-one (**B-2**, *vide infra*). A consistent structure is bicyclo[3.2.2]nonan-6-one (**B-3**).[51]

(3) *Deuterium exchange in hydrogenation products* A *and* B (**B-3**). When the unresolved product of the hydrogenation of 30 mg VI (as in 2) dissolved in 50µl. dioxan was added to a mixture of 1 ml dioxan and 1 ml D_2O containing 20 mg dissolved Na metal and allowed to stand for 7 hr, samples of ketones A and B (as in 2 above) could be recovered by ether extraction and separated by GLPC. Whereas ketone A had an IR spectrum indistinguishable from A above, the second ketone (B; 1715 cm^{-1}) showed C-D absorption in the IR at 2205 and 2125 cm^{-1}.

(4) *Hydrogenation of tricyclo*[3.3.1.$0^{2,8}$]*nonan-9-one* (**B-2**). A soln of 0·500 g tricyclo[3.3.1.$0^{2,8}$]nonan-9-one[22] in 20 ml EtOH was hydrogenated over 10% Pd–$CaCO_3$ (100 mg) until hydrogenation (1 equiv) was complete. Following the addition of 30 ml n-hexane, the azeotrope of EtOH and n-hexane was removed by careful distillation through a 20-cm column packed with a nichrome coil. GLPC on a 5-ft Carbowax 4000 column (20% on 50–60 mesh Anakrom ABS at 130°) showed one major product (96%; rel ret time 1·47) and a minor product (4%; rel ret time 1·00). The IR spectrum of the major product is identical with that of the ketone B (**B-3**) from the hydrogenation of barbaralone (VI; see 2 above).

Tricyclo[3.3.1.$0^{2,8}$]*nona-3,6-dien-9-ol* (**E-1**)

(a) *Reduction of* VI. VI (2·5 g) in MeOH (150 ml) with $NaBH_4$ (0·750 g) in MeOH (90 ml) at room temp for 24 hr afforded 2·10 g crystalline product after removal of MeOH, dilution with 50 ml 10% $NaHCO_3$aq, extraction with three 100-ml portions of ether and concentration of the dried ethereal extract. Pure tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-ol (**E-1**) was obtained as colorless plates by crystallization from pentane; m.p. 88–90°.

The NMR spectrum at 25° consisted of two triplets each of area 1 at δ = 6·00 and 5·65 ppm; a broad doublet of area 4 centered at δ = 3·98 ppm; a triplet of area 1 at 3·52 ppm; a multiplet of area 2 at 2·49 ppm; and a singlet of area 1 at 1·38 ppm.

Attempts to obtain the corresponding carbonium ion (**E-4**) by treatment of the alcohol **E-1** with 96% H_2SO_4, with SbF_5 and with BF_3 in CH_2Cl_2 were unsuccessful.

(b) *9-Chlorotricyclo*[3.3.1.$0^{2,8}$]*nona-3,6-diene* (**E-2**). The corresponding chloride **E-2** was obtained from the carbinol **E-1** by treatment with $SOCl_2$ and pyridine. A soln of 0·93 g of **E-1** and 0·56 ml of anhyd pyridine in 15 ml anhyd ether in a 2-necked flask equipped with a magnetic stirrer, a condenser with drying tube and a serum cap was cooled to −10°. A 0·5 ml sample of $SOCl_2$, which had been freshly distilled from quinoline, was injected over a 10-min period through the serum cap with a syringe. The resultant ppt was stirred for 3·5 hr at −10° and then allowed to warm to room temp over another hr.

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[51] Although bicyclo[3.2.2]nonan-6-one is reported in the literature (m.p. 170°), the only derivative reported is the semicarbazone which unfortunately does not melt but decomposes.[38]

The filtered soln was washed successively with 15 ml 10% $NaHCO_3$aq, 10 ml water and 15 ml sat NaClaq. The dried ($MgSO_4$) ethereal soln was concentrated to a residue which was recrystallized from n-hexane to give 400 mg (30%) 9-chlorotricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene (**E-2**), m.p. 105–106° (NMR spectrum: three triplets each of area 1 at δ = 5·73, 5·55 and 4·40 ppm; a triplet at 4·00 ppm of rel. area 4 and a multiplet of rel. area 2 at 2·56 ppm).

According to the procedure of Olah *et al.*,[35] SbF_5 was added dropwise to a soln of the chloride **E-2** in liquid SO_2 at −30° in an NMR tube. Discoloration and precipitation resulted and no NMR spectrum could be observed.

Following the procedure of Katz and Gold,[36] the chloride **E-2** was dissolved in liquid SO_2 at −70° together with silver hexafluoroantimonate, shaken for 1·5 hr, filtered and placed in an NMR tube at 0°. Only the signals of unreacted chloride could be seen.

(c) *9-p-Toluenesulfonoxytricyclo*[3.3.1.$0^{2,8}$]*nona-3,6-diene.* A soln of 495 mg of the carbinol **E-1** in 2 ml anhyd pyridine was treated with 720 mg freshly recrystallized *p*-toluenesulfonyl chloride at 0°. After 12 hr at room temp and 5 days at 0°, the mixture was poured into ice water and extracted 4 times each with 20 ml ether. The combined ethereal extracts were washed 3 times each with 10 ml 20% H_2SO_4aq, twice each with 15 ml water, twice each with 25 ml 2% $NaHCO_3$aq and twice each with 10 ml water. Removal of ether left 150 mg of a yellow oil which showed no OH absorption in the IR, but the absorptions at 2855, 1357, 1180 and 820 cm^{-1} characteristic of *p*-toluenesulfonate esters.[52]

Upon standing in 12·5 ml glacial AcOH containing 71·7 mg AcONa for 72 hr at room temp, the tosylate (141 mg) was recovered with unchanged IR spectrum.

Upon being heated in a similar solution for 72 hr at 65°, the tosylate reacted to give a product shown by analysis on a 3-m Dow-Corning 710 silicone oil (15% on kieselguhr) column to consist of one major and two minor (unidentified) components. Reduction with LAH in ether at room temp of the reaction product (80 mg) afforded **E-1** (IR spectrum identical with that of authentic material).

Tricyclo[3.3.1.$0^{2,8}$]*nona-3,7-diene* (*barbaralane*, VII)

(a) *Preparation by Wolff Kishner reduction of barbaralone* (VI). A mixture of 400 mg VI, 1·5 g 85% hydrazine hydrate and 2 g KOH in 3 ml diethylene glycol was heated for 1 hr at 110–115° and then for 3 hr at 170–180°. About 150 mg crystals appeared in the water-cooled condenser. Dissolved in CCl_4, dried over $MgSO_4$ and analyzed on a 2-m column of Carbowax 20 M (15% on kieselguhr) at 114° and 14 lb He, this product was found to consist of three compounds: A (rel ret time 1·00; 20%); B (rel ret time 1·41; 50%); and C (rel ret time 1·92; 30%). On the basis of spectral evidence compound C, m.p. 30–31°, is assigned structure VII. It has *inter alia* absorption in the IR at 3045, 2952, 2920, 2862, 1618 and 701 cm^{-1}. The NMR is quite similar to that of VI: a triplet of rel area 2 centered at δ = 5·62 ppm (J = 7·3 c/s) in which each arm is further split into a triplet (J = 1·9 c/s); a triplet (complicated) of relative area 4 centered at 3·90 ppm (J = 7·1 c/s); a multiplet centered at 2·27 ppm of rel area 2 and a triplet at 1·03 ppm of rel area 2 (J = 2·5 c/s); Although the reported m.p. 46° is higher than that obtained here, the IR and NMR spectra are in good agreement.[34]

Compound A is characterized by an IR spectrum (3040, 3022, 2934, 2872, 2865, 2829, 1630, 1460, 884, 710 and 680 cm^{-1}) and an NMR spectrum in which the ratio of olefinic to paraffinic protons is 4:6.

Compound B is characterized by its IR spectrum (3040, 3017, 2951, 2924, 2875, 2818, 1629, 1608, 862, 710 and 680 cm^{-1}) and NMR spectrum [triplets at δ = 6·49 and 6·08 ppm (superimposed on a multiplet) (rel area 5); multiplets at 4·94 (1), 2·91 (2) and 2·04 ppm (2)].

(b) *Temperature dependence of the NMR spectrum of* VII. The low-temperature spectra were measured on the Varian HR-60 NMR spectrometer.[53] The line-width at half-height of the resonance centered at δ = 3·90 ppm is shown as a function of temp in Table 1. At high temp this resonance is a triplet (J = 7·1 c/s) while at low temp it is separated into two triplets each of rel area 2 separated by 205·4 c/s. These triplets represent the pair of cyclopropyl hydrogen atoms and the pair of vinyl hydrogen atoms, adjacent to bridgehead H-atoms. Each H-atom of the two pairs is spin-spin coupled to an adjacent olefinic H-atom in the center of the molecule and an adjacent bridgehead H-atom. Since all four coupling constants are fortuitously nearly equal, the spacing of the high and low field triplets is approximately the same.

The high temp triplet reflects the degenerate rearrangement which interchanges the pairs of cyclopropyl and olefinic H-atoms. Each arm of this triplet is split into a further fine triplet by coupling across the ring

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[52] R. S. Tipson, *J. Am. Chem. Soc.* **74**, 1354 (1952).

[53] We wish to express our thanks to Mr. R. B. Holt, Yale University, for these measurements.

At the intermediate temps the resonance has a broad shape, but at 202·0 and 204·0°K the triplet character has clearly emerged

The rates were obtained by the method of comparison of the experimental spectra at each temp with spectra calculated by a general computer program which simulates as many of the circumstances surrounding the experimental spectra as possible.[42,54] Owing to spin-spin coupling, a calculation of line-shape based on two sites is inadequate and has been replaced by a model based on 6 sites with probabilities 1:2:1:1:2:1 to simulate the pair of 1:2:1 triplets in the low temp spectrum. In this model lines 1 and 4, 2 and 5, and 3 and 6 are then interchanged by the degenerate rearrangement. In order to approximate the additional width due to unresolved fine structure in the spectra at high temp,[54] the natural line-width parameter was evaluated by empirical variation and comparison with the high temp spectra, with the aid of approximate rates determined from the observations at lower temps. The value which brought the two higher temp observations onto the line of the plot of calculated rate against the reciprocal of temp was selected (T_2 = 0·1 sec) for the recalculation of all line shapes to determine the final rates shown in Table 1.

TABLE 1. TEMPERATURE DEPENDENCE OF THE NMR SPECTRUM OF TRICYCLO-[3.3.1.0^{2,8}]NONA-3,7-DIENE (VII)

Δ[*]	Temp in °K	$10^3\,T^{-1}$	Rate (R) in sec^{-1}	ln R
41·80	184·0	5·43	1945	7·573
30·80	187·0	5·35	2980	8·000
28·10	188·0	5·32	3475	8·153
22·70	192·0	5·21	5445	8·602
21·15	193·5	5·17	7120	8·871
19·30	196·0	5·10	9000	9·105
17·35	199·5	5·01	13,500	9·510
17·10	202·0	4·95	16,000	9·680
16·30	204·0	4·90	20,000	9·903

[*] Δ is the line width in cycles per second measured at half-height of the absorption at δ = 3·90 ppm

Another program was used to fit these rates to the Arrhenius equation by the method of least-mean-squares and to calculate the standard deviations. The result is an activation energy, E_a = 8·6 ± 0·2 kcal/mole, and a frequency factor, A, where log A = 13·6 ± 0·3. The 90% confidence limit of the activation energy is estimated to be ±1 kcal/mole.

Conversion of tricyclo[3.3.1.0^{2,8}]*nona-3,6-dien-9-one* (VI) *to bullvalone* (V)

(a) 9-*Aldehydotricyclo*[3.3.1.0^{2,8}]*nona-3,6-diene* (**F-1**). A soln of diazomethane in ether (4 ml of a soln prepared from 1 g N-methyl-N-nitrosourea and 20 ml ether) was added at 0° with stirring to a soln of 100 mg VI and 20 mg KOH in 2 ml MeOH. After 2 hr at 0° and 10 hr at room temp, the mixture was concentrated and analyzed on a 5-ft column (20% of Carbowax 20 M on kieselguhr at 145° and 20 lb H_2) to reveal an easily separable major product (65%; rel ret time 1·00), starting material (20%; rel ret time 1·60) and a ketone (15%; rel ret time 2·05).

The major product, which is assigned the structure, 9-aldehydotricyclo [3.3.1.0^{2,8}]nona-3,6-diene (F-1), gives a semicarbazone, m.p. 194–195° w. dec, when 15 mg aldehyde in 0·5 ml EtOH is added to 30 mg semicarbazide hydrochloride and 50 mg AcONa in 1 ml water. (Found: C, 65·6, 64·9; H, 6·4, 6·4; N, 19·8. $C_{11}H_{13}N_3O$ requires: C, 65·0; H, 6·5; N, 20·7%.) NMR spectrum: δ = 9·44 ppm (doublet of area 1); 5·7 ppm (two overlapping triplets of area 2); 4·1, 4·0 ppm (superficially a doublet of area 4); 2·7 ppm (multiplet of area 2); 1·9 ppm (multiplet of area 1). The crude product *before* passing through the GLPC column shows none of the IR bands characteristic of the aldehyde, which thus appears to result from the rapid rearrangement of the epoxide on the column.

[54] M. Saunders in *Proceedings of Conference on Application of Magnetic Resonance to Biology*, p. 85. Stockholm, Pergamon Press (1966).

(b) *Tricyclo*[3.3.2 0^{2} ^{8}]*deca-3.6-dien-9-one* (V. *bullvalone*). The ketone in (a) above is obtained in somewhat better yield by the following modified procedure in which alkali is not present in the reaction.

To 1·8 g VI dissolved in 36 ml MeOH there was added at 0° 120 ml of a soln of diazomethane [prepared from 8 g of N-methyl-N-nitrosourea, 14 ml of 50% KOH aq and 130 ml ether, and dried over KOH pellets for few min]. The reaction vessel was placed into a 1·5 gal cooling vessel filled with ice, covered with Al foil and allowed to stand for 18 hr. The soln was concentrated first to about 80 ml by evaporation under reduced press and then by distillation at high reflux ratio through a column packed with stainless steel wool with the bath temp not exceeding 135°. About 3 4 ml of MeOH was finally removed by short evacuation. The crude product, 2 g, could be most conveniently separated by GLPC on a 5-ft column of diethyleneglycolsuccinate (20%) on Chromosorb W at 155° using 18 lb He press (injection block at 175°) to elute the aldehyde and 10 11 lb He press to elute the ketone in order to avoid aerosol formation in the collection receiver. The aldehyde (**F-1**) (rel ret time 1·0) is obtained in 24% of theory (484 mg) whereas the ketone V (rel ret time 3·0) is obtained in 25% of theory (500 mg); m.p. 36–37° after one crystallization from pentane.

The UV spectrum of V shows only tailing which vanishes around 275 mμ. The IR spectrum in CCl_4 shows the following bands in cm^{-1}: 3040 (very strong); 2935 (s); 2900 (medium); 1685 (vs); 1392 (s); 1380 (s); 1365 (s); 1351 (s); 1342 (s); 1259 (s); 1220 (m); 1168 (s); 1088 (m); 1066 (m); 986 (m); 957 (m); 919 (s); 878 (s); 827 (m); 710 (s); 678 (m). The NMR spectra are complicated and are recorded here on the δ scale in ppm as an aid to identification, incompletely and with relative peak height despite the comparative uselessness of such numbers. The ratio of areas of vinyl absorption to other hydrogens is 4:6 at high and low temp. The spectrum at +90°: 6·10 (0·7); 5·93 (1·8); 5·83 (4·9); 5·67 (3·5); 5·50 (1·1); 2·70 (2·3); 2·54 (3·9); 2·37 (10·0); 2·32 (5·5). The spectrum at −27·5°: 6·01 (5·4; a broad peak between 6·09 and 5·85 ppm); 2·85 (1·2); 2·69 (2·5); 2·55 (4·0); 2·33 (10·0); 2·26 (6·6).

(c) *Reaction of diazomethane with the malononitrile adduct of* VI. In an effort to reduce the amount of aldehyde (epoxide) produced in the reaction of VI with diazomethane, an attempt to employ the malononitrile adduct was made, based on the analogous work of Bastús.[37] The unpurified product of 100 mg VI and 56 mg malononitrile (*vide supra*) in 1 ml MeOH was treated with 5 ml of an ethereal diazomethane soln (from 700 mg N-methyl-N-nitrosourea and 10 ml ether). After 3 min volatile material was removed *in vacuo* and the residue was steam-distilled. Extraction with ether of the distillate and concentration afforded 60 mg of product which consisted of a small amount (ca. 10%) of V and a large amount of unreacted VI.

This procedure has also been applied to the conversion of cycloheptanone to cyclooctanone. After 2 hr at 25°, a mixture of 2·0 g malononitrile, 3·8 g cycloheptanone and 0·05 ml pyridine was shaken with 20 ml benzene, 7·5 ml water and 2·5 ml 2N HCl. The benzene layer was washed with 4 10 ml portions of water and distilled to give 3·35 g cycloheptylidene malononitrile, b.p. 90° 0·18 mm.

This material in 10 ml MeOH at 0° was treated with 35 ml ethereal diazomethane [from 4·6 g N-methyl-N-nitrosourea, 9 ml 50% KOH and 55 ml ether]. After an initial vigorous evolution of N_2, the soln remained at 25° for 12 hr and was concentrated. The residue was added to 20 ml 30% NaOH aq and steam-distilled to give 2·10 g of product which consisted (95%) of cyclooctanone (identified by IR spectrum).

Reduction of bullvalone V

(a) *Hydrogenation with platinum*. A soln of 13·1 mg V freshly purified by GLPC in 1·25 ml glacial AcOH and a mixture of 30 mg prereduced PtO_2 in 5·5 ml glacial AcOH were shaken with H_2 at 26° for 17 min when absorption was complete (3·15 molar equiv). After an additional 30 min of shaking, the soln was diluted with 15 ml H_2O and extracted with 10 ml ether. The ethereal soln was washed with 10% Na_2CO_3 aq, dried and concentrated to a residue which was found by GLPC on a 3-m Carbowax 20 M column to consist of 4 pts of a ketone (rel ret time, 1·00; m.p. 178°; IR: 1690; 1463; 1449; 1348; 1180 cm ^{1} among other weaker bands) and 1 pt of an alcohol (rel ret time 1·44; m.p. 155°; IR: 3630; 3380 (very broad)). The ketone has a parent peak in the mass spectrum, *m e* 152, and an NMR spectrum with three broad bands at 2·40, 2·00 and 1·73 ppm. The relative area at the resonance about 2·50 ppm cannot be measured with high accuracy but certainly agrees better with a ratio of 4:12 than 3:13. The ketone is presumed to be bicyclo-[3.3.2]decan-3-one[55] and not the decan-9-one or 2-one; but the point is not settled.

(b) *Reduction of bicyclo*[3.3.2]*decan-3-one*. The ketone in (a) above (135 mg) and 150 mg hydrazine hydrate, 200 mg KOH and 1 ml trimethyleneglycol was heated over a 3-hr period from 68–188° in a flask with distillation head. After 5 hr at the highest temp, the cold finger, on which semisolid had collected, was

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[55] Bicyclo[3.3.2]decan-3-one is reported with no m.p. but a semicarbazone, m.p. 212 213° with dec.[38]

washed with 0·5 ml ether. Analysis of the crude product (86 mg) by GLPC showed one major product: m.p. 167·5° (taken in the collection tube without further purification). It had the same retention time and IR spectrum as the hydrocarbon VIII from the catalytic reduction of bullvalene (*vide infra*).

(c) *Reduction of tricyclo*[3.3.2.0^{2,8}]*decan-3-one* (F-3). A soln of 200 mg F-3[22] in 10 ml glacial AcOH containing 75 mg PtO_2 was completely hydrogenated in 2 hr. Filtration, dilution with 10 ml H_2O, addition of enough 20% KOH to make basic, extraction with three 50-ml portions of ether, drying over $MgSO_4$ and concentration by distillation through a 20-cm column packed with nichrome coil afforded crude ketone. A mixture of this ketone, 0·25 g KOH and 0·25 g 85% hydrazine hydrate in 1·2 ml triethyleneglycol was heated at 185° for 5·5 hr in a flask fitted with condenser. Diluted with 3 ml water, the reaction mixture was extracted with six 15-ml portions of ether. The dried (KOH pellets) ethereal extract was concentrated by careful distillation to a residue, from which a major product (VIII) was isolated by GLPC (5-ft 20% silicone 710 on 50–60 mesh Anakrom ABS at 140°): m.p. 179–180°. Its IR spectrum is identical with those of the hydrocarbons obtained from bullvalone (*vide supra*) and from bullvalene by hydrogenation (*vide infra*). The IR spectrum follows: 2920 (very strong); 2725 (weak); 2700 (medium); 2670 (w); 1480 (m); 1460 (s); 1445 (s); 1365 (m); 1330 (vw); 1300 (vw); 1225 (m); 1190 (vw); 1165 (m); 1055 (m); 1030 (w); 970 (vw); 945 (vw); 930 (vw); 920 (vw); 900 (vw); 870 (m)

Deuterium exchange in bullvalone (V)

(a) *Mass spectrum of bullvalone.* At an ionization potential of 68 v., bullvalone showed the following prominent peaks (*m/e*) with their relative intensities: 147 (6·1); 146 (51·4; parent); 145 (10·4); 119 (5·2); 118 (51·0; minus CO); 117 (84·8; minus HCO); 116 (8·9); 115 (23·1); 104 (100; minus C_2H_2O); 103 (46·0); 102 (7·2); 91 (43·4); 78 (50·6); 77 (20·8); 65 (18·6); 63 (20·9); 52 (14·6); 51 (33·1); 50 (20·4); 39 (49·6).

Analysis for deuterium content was effected at a lower ionization potential (15 v) where the contribution of fragments of *m/e* below the 102–104 range is much reduced. Calculation of distribution of deuterium was based on the parent peak corrected for ^{13}C concentration.

(b) *Deuterium exchange after longer times of reaction.* A soln of 21·4 mg bullvalone in 0·642 ml of a D_2O (100 pts): dioxan (75 pts) mixture 0·4N in NaOD was allowed to stand at 29–30°. After periods of 9, 18

concentrated ethereal extracts were purified by GLPC (2-m, ¼ in. column 20% diethylene glycol succinate on 40–60 mesh kieselguhr at 157°). Each sample is analyzed by mass spectrography with the following results—9-hr reaction: D_0 (0·1), D_1 (0·4), D_2 (1·8), D_3 (6·3), D_4 (14·6), D_5 (23·3), D_6 (25·0), D_7 (17·6), D_8 (8·1), D_9 (2·3), D_{10} (0·5%); 18-hr reaction: D_0 (0·0), D_1 (0·0), D_2 (0·8), D_3 (1·7), D_4 (3·2), D_5 (7·4), D_6 (15·5), D_7 (23·6), D_8 (25·5), D_9 (16·7), D_{10} (5·6%); 35·5-hr reaction: D_6 (0·0), D_7 (1·4), D_8 (16·3), D_9 (40·8), D_{10} (41·3%).

There is some decomposition in alkali as evidenced by the gradual development of a brown color and the appearance of a new ketone in the gas chromatogram. After 24 hr in 0·4 N NaOH, this product amounts to 18% of the total: IR at 1653 cm^{-1}; λ_{max} 226 mμ (log ε 3·67 in hexane).

(c) *Deuterium exchange after shorter times.* In these experiments an even lower ionizing potential was employed (7·8 v.) where the mass spectrum, corrected for ^{13}C isotope, consisted of *m/e* 146 (parent, 69·2%) and *m/e* 118 (30·8%).

In the same manner as outlined above in (b), but at 24°, 30·0 mg V in 0·860 ml 0·4N NaOD in D_2O-dioxan (100:75) was allowed to react for 0·5, 1 and 4 hr and aliquots (0·200 ml) were analyzed (isolation of bullvalone on 5-ft ¼ in. 20% silicone (GE-SF-96) on 60–80 firebrick at 135° and 20 lb He). After each analysis of partially deuterated V, undeuterated V was analyzed to confirm the absence of any instrumental memory—0·5-hr reaction: D_0 (1·2), D_1 (8·0), D_2 (74·0), D_3 (13·8), D_4 (2·1), D_5 (0·4%); 1·0-hr reaction: D_0 (1·0), D_1 (6·3), D_2 (60·9), D_3 (24·7), D_4 (5·7), D_5 (1·1%); 4-hr reaction: D_0 (0·7), D_1 (4·0), D_2 (31·3), D_3 (35·1), D_4 (20·0), D_5 (6·6), D_6 (1·9), D_7 (0·4%).

Conversion of bullvalone (V) *to bullvalene* (I)

(a) *Reduction of* V *with sodium borohydride.* Bullvalone (V, 50 mg) in 0·5 ml EtOH was added at 0° to 60 mg $NaBH_4$ in 1·5 ml EtOH. Over a period of 18 hr the mixture gradually warmed to room temp. After evaporation of methanol, treatment with 3 ml 20% Na_2CO_3aq, warming to 55° for 10 min and extraction with two 5-ml portions of ether, an ethereal extract was obtained, which was concentrated to give 29 mg liquid 9 (or 10)-hydroxytricyclo[3.3.2.0^{2,8}]deca-3,6-diene. Homogeneous by GLPC, this alcohol has an

IR spectrum in CCl_4 with the following bands: 3600, 3380, 3035, 2932, 1648, 1625, 1408, 1288, 1262, 1215, 1201, 1088, 880, 850, 726, 711, 699, 676 cm^{-1}.

(b) 9 (*or* 10)-*Acetoxytricyclo*[3.3.2.$0^{2,8}$]*deca*-3,6-*diene* (**F-4**). A soln of 25 mg carbinol (a above) in 0·25 ml pyridine was mixed with 0·10 ml Ac_2O, refluxed for 15 min at 130°, poured into 2·5 ml H_2O, allowed to stand for 15 min and extracted 3 times, each with 1 ml ether. Drying and concentration afforded 22·5 mg 9(or 10)-acetoxytricyclo[3.3.2.$0^{2,8}$]deca-3,6-diene (**F-4**) as an uncrystallized oil.

(c) *Tricyclo*[3.3.2.$0^{2,8}$]*deca*-3,6,9-*triene* (I, *bullvalene*). Pyrolysis of **F-4** was effected in a Pyrex tube 5·5 cm long and 7 mm i.d. filled with glass helices and heated electrically. While N_2 was passed through the tube at a rate of 0·67 ml/sec, a 10% soln of the acetate in ether was dropped in slowly at the top and the products were collected in a Dry-Ice trap at the bottom. At an inside temp of 345°, two major products were formed. Analyzed by GLPC on a 5-m ¼ in. column containing 5% Carbowax 20M on 40-60 mesh kieselguhr at 108°, bullvalene of rel ret time 1·00 and *cis*-9,10-dihydronaphthalene (IX) (*vide infra*) of rel ret time 0·386 were isolated in about equal quantity. At an inner temp of 440° the yield of I and IX decreased at the expense of five additional products. Bullvalene, isolated by GLPC, melted at 93° (m.p. 93° in a mixture with a sample of authentic material, m.p. 93°, synthesized according to Schröder[16,39]) and had IR and NMR spectra identical with those of authentic material. The mass spectrum of bullvalene at 68 ev consists of the following peaks with their relative intensities: *m/e* 131 (7·1); 130 (70·4); 129 (100·0); 128 (74·6); 127 (33·1); 126 (3·6); 116 (5·5); 115 (53·3); 103 (6·3); 102 (8·6); 91 (4·1); 89 (3·3); 78 (6·3); 77 (9·6); 76 (3·2); 75 (3·4); 74 (3·7); 65 (5·5); 64·5 (2·6); 64 (11·5); 63·5 (3·1); 63 (10·4); 62 (3·6); 52 (6·1); 51 (18·9); 50 (10·0); 39 (15·6); 38 (4·2); 27 (6·0); 26 (3·7).

Catalytic reduction of bullvalene (I)

A soln of 100 mg bullvalene (I), synthesized according to Schröder,[39] in 20 ml AcOH containing 55 mg of Adams PtO_2 absorbed 3·8 molar equivalents of H_2 in 2·5 hr at room temp. The filtered soln was diluted with 50 ml pentane and extracted with three 50-cc portions of water. Drying over KOH pellets and distillation through a 20-cm Vigreux column left a residue which was analyzed by GLPC on a 5-m column, 20% silicon oil #710 on 50/60 Anakrom ABS at 140°. The major product (81%) of rel ret time, 1·00, was isolated and identified as VIII by the complete identity of IR spectra (*vide supra*). The structure of the minor product (19%; rel ret time 0·893) has not been established. The ratio of the two products becomes 1:1 when the hydrogenation is effected in ethanol over 2% Pd–$CaCO_3$.

Reaction of bullvalene with perphthalic acid

(a) A soln of 766 mg (5·9 mmole) bullvalene and 5·0 mmole perphthalic acid in 43·5 ml $CHCl_3$ was allowed to stand at −5° for 2 hr when the peracid had been consumed. Filtration and concentration *in vacuo* under N_2 gave a residue. Unreacted bullvalene was removed by crystallization at −78° from 32 ml hexane. The recovered crude product showed absorption in the NMR: a doublet at $\delta = 9·87$ ppm, complex absorption at 6·75 and 6·25, and two doublets centered at 5·05. In the IR, there was strong carbonyl absorption at 1720 and 1680 cm^{-1}, and strong absorption at 825, 700 and 640 cm^{-1}. The crude product polymerized at room temp.

(b) Catalytic hydrogenation of the residue in 8 ml AcOEt with 100 mg 5% Pd/C afforded a crude product which could be separated by GLPC on a 5% Carbowax column into an aldehyde (IR spectrum: 2870, 2718, 1730, 1460, 1448, 1408 and 1382 cm^{-1}) and an alcohol (IR spectrum 3630 cm^{-1} and a broad band centered at 3400).

cis-9,10-*Dihydronaphthalene* (IX)

(a) *Pyrolysis of bullvalene* (I). When a soln of 870 mg bullvalene in 6 ml ether was added dropwise to the pyrolysis apparatus and carried through the column at 380° by a stream of N_2, a blue-brown mixture of products was obtained which could be separated by GLPC on a column ¼ in by 12 ft containing 20% diethyleneglycolsuccinate at 98°. The major product (ca. 85%) was *cis*-9,10-dihydronaphthalene identified by comparison of its NMR and UV [λ_{max} 222 mμ ($\varepsilon = 3945$); 248 mμ ($\varepsilon = 4072$) in hexane] spectra with those reported by van Tamelen and Pappas.[40] Aside from naphthalene none of the minor products was isolated.

(b) *Catalytic hydrogenation.* When 18·2 mg *cis*-9,10-dihydronaphthalene in 6 ml THF was treated with H_2 in the presence of 200 mg of 2% Pd/$CaCO_3$, no H_2 was absorbed. Separation by GLPC afforded naphthalene and 1,2,3,4-tetrahydronaphthalene, both identified by the identity of their IR spectra and retention times with those of authentic materials.

Methylbullvalene

(a) *9-Hydroxy-9-methyltricyclo*[3.3.2.0^{2,8}]*deca-3,6-diene*. A soln of 400 mg bullvalone (V) in 3 ml abs ether was added dropwise at 0° with stirring under N_2 to 9 ml of a 0·5 N soln of MeLi prepared according to Müller and Ludsteck.[56] After 8 hr, a mixture of 5 ml MeOH and 15 ml ether was added, followed by 15 ml water. Extraction with three 25-ml portions of ether, washing the combined ethereal extracts with water, concentration to 3 ml and separation in a 2-m column 20% in diethyleneglycolsuccinate at 160° afforded 197 mg (45%) 9-hydroxy-9-methyltricyclo[3.3.2.0^{2,8}]deca-3,6-diene, m.p. 46-48°, and 40 mg unreacted bullvalone.

(b) *Methylbullvalene*. A soln of 190 mg of the tertiary carbinol above in 0·38 ml ether was injected in 0·03 ml portions into a 5-ft, ¼ in column containing 20% diethyleneglycolsuccinate on Chromosorb W with the injection block at 320° and a flow rate of 1 ml He per sec. The crude methylbullvalene (135 mg, 79%) was purified by GLPC on the same column at 120°. The pure liquid had an IR spectrum with prominent bands at 3060 cm^{-1} (vs), 2967 (s), 2930 (s), 2883 (w), 2856 (w), 1539 (s), 1440 (s), 1403 (m), 1368 (m), 1310 (w), 1134 (w), 1080 (m), 891 (m), 872 (s), 857 (s), 841 (m), 830 (m), 722 (s), 698 (s), 648 (s), 630 (m).

The NMR spectrum in CCl_4 at −40·0° consisted of a singlet at δ = 1·75 ppm (rel area 3·02), and broad bands at 2·00 (rel area 3·85), at 5·53 and 5·62 ppm (total rel area 5·00). At 97·5°, the time averaged spectrum was observed: a sharp singlet at 1·71 ppm (rel area 1·07) and another sharp singlet at 4·04 ppm (rel area 3·00).

The mass spectrum at 68 ev consisted of the following peaks (omission of those of intensity less than 5% of the peak at *m/e* 129): *m/e* 144 (16·0%); 143 (14·4); 142 (8·1); 141 (10·0); 130 (10·7); 129 (100·0); 128 (71·0); 127 (23·7); 115 (16·3); 91 (5·2); 77 (6·5); 63 (6·5); 51 (9·6); 39 (11·9); 27 (5·8)

Phenyltricyclo[3.3.2.0^{2,8}]*deca-3,6,9-triene*

A soln of 270 mg XIV in 1 ml abs ether is added in a N_2 atmosphere to 3 ml of a Grignard reagent prepared from a mixture of 1·55 g Mg and 9·05 g bromobenzene in 23 ml ether. After 16 hr, the mixture was treated with 3 ml conc. NH_4Cl aq. 10 ml H_2O and extracted with ether. Concentration of the dried ($MgSO_4$) ethereal extract afforded a residue which could be purified by GLPC on a 5-ft, ¼ in column of glass micro-beads coated with silicone rubber (0·25% by wt.) at 155° (injection block at 174°). The resulting carbinol, m.p. 72-74°, showed OH absorption at 3548 cm^{-1} (s), and bands *inter alia* at 3222 (vs), 2920 (s), 1638 (m), 1600 (m), 1490 (s), 1446 (s), 1369 (s), 1314 (s), 1259 (m), 1168 (s), 1057 (s), 1041 (s), 1028 (s).

TABLE 2. IR ABSORPTION IN BULLVALENE AND METHYL- AND PHENYLBULLVALENE

Bullvalene ν in cm^{-1}	Methyl-bullvalene ν in cm^{-1}	Phenyl-bullvalene ν in cm^{-1}
3038	3031	3032
2971	2968	2970
2944	2930	—
1634	1639	1638
1400	1403	1402
1363	1360	1370
1309	1310	1309
1076	1080	1078

When 165 mg of the crude product was passed over a 5-ft, ¼ in column, 7% Carbowax 4000 on 50-60 mesh Anakrom, at 190° (injection block 200°), 27·4 mg phenylbullvalene (rel ret time 1·00) was obtained. Bullvalene (30%, rel ret time 0·23), diphenyl (20% rel ret time 0·108) and three unidentified products were also obtained. Final purification of the phenylbullvalene on the 0·25% silicone rubber column afforded material, m.p. 53-54°, which still retained a faint blue colour; λ_{max} 255 mμ (log ε = 3·90) [reported[47] m.p. 74-76° from EtOH; λ_{max} 262 mμ (log ε = 3·93)].

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[56] E. Müller and D. Ludsteck, *Chem. Ber.* **87**, 1887 (1954).

NMR spectra of phenylbullvalene were obtained in CS_2 at −35·0° (singlet at δ = 7·07 ppm; broad absorption centered at 5·73; broad absorption at 2·74 and 2·20 of rel areas 5·1 : 5·0 : 3·8, respectively) and at 70° (singlet at δ = 7·07 ppm and a broad singlet at 4·27 ppm of relative areas 5·0 : 8·1, respectively).

The IR spectrum showed bands *inter alia* at 3032 cm^{-1} (vs), 1638 (m), 1598 (m), 1488 (m), 1443 (m), 1402 (m), 1370 (m), 1030 (m), 888 (m), 871 (m), 841 (m), 697 (vs), 643 (s). Coincidences in IR bands in bullvalene, methylbullvalene and phenylbullvalene are shown in Table 2.