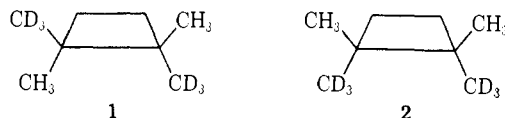the trans isomer was achieved by use of optically active *trans*-1,2-dimethyl-1,2-bishydroxymethylcyclobutane as an intermediate, the diol being partially resolved by fractional crystallization of the diastereomeric mixture of *d*-mandelates. Optically pure *trans*-hydrocarbon **1** was shown to have $[\alpha]_{546}$ 1.21° (CS$_2$) (enantiomeric configuration arbitrary).

Infrared analysis (Perkin-Elmer Model 421 spectrometer), using absorptions at 1370, 1355, 1075, and 920 cm^{-1}, permitted estimation of *trans*- and *cis*-hydrocarbons **1** and **2** to ±10% and detection of as little as 10% of one isomer in the other.

Pyrolysis of tetramethylcyclobutane-d_6 (**1** or **2**) in an "aged" reactor at temperatures in the range 338–401° and initial pressures between 10 and 30 mm gave isobutylene-d_3 as the major product (>99%).[6]

Tetramethylcyclobutane-d_6 recovered from varying degrees of partial pyrolysis of pure trans (or cis) hydrocarbon showed no detectable quantity (<10%) of the cis (or trans) isomer, even after 96% decomposition to isobutylene. Moreover, optically active d_6-*trans*-hydrocarbon **1** was recovered from partial pyrolysis with undiminished activity (racemization <4% after 11.7% decomposition).

Configurational inversions of each of the substituted carbons C$_1$ and C$_2$ of tetramethylcyclobutane plausibly (but not necessarily) might be achieved by rotations about the C$_1$–C$_4$ or C$_2$–C$_3$ bond axes. In the most general sense, if the number of such inversions of C$_1$ is r and that of C$_2$ is s, $(r + s)$ *odd* corresponds to the reaction trans $\rightleftharpoons$ cis, and $(r + s)$ *even*, r and s both odd, corresponds to the reaction (−)-trans $\rightleftharpoons$ (+)-trans. The experimental results show that regardless of mechanistic details, both such processes are indetectably slow relative to fragmentation. The upper limits for the amount of racemization of (−)-**1** and for the amount of conversion to **2** may be combined with the overall per cent decomposition to give minimum values for the ratio of the rate constant for the decomposition, trans → 2-isobutylene (k_d), to that for enantiomerization, (−)-trans → (+)-trans (k_e), or geometric isomerization, trans → cis (k_i). The ratios are derived from the relationship of eq 1,[7,8] where $f_t, f_c, f_-,$ and f_+ represent

$$1 + \frac{2k_i}{k_d} = \frac{\log (f_t - f_c)}{\log (f_t + f_c)} = \frac{\log (f_- - f_+)}{\log (f_+ + f_-)} = 1 + \frac{2k_e}{k_d}$$

(1)

the fractions of trans, cis, −, and + components, respectively. These ratios are $k_d/k_e \geqslant 6$ (at 360°) and $k_d/k_i \geqslant 22$ (at 401°).

Although not obligatory, it is convenient to discuss

(6) Traces of tetramethylethylene-d_6 and ethylene also were observed. In an unconditioned reactor packed with glass beads, prolonged pyrolysis again produced mainly isobutylene, together with traces of tetramethylethylene, but two minor unidentified products also appeared. At least one of the latter products showed nmr absorption consistent with a terminal methylene group and may have been formed by transfer of hydrogen from a methyl group.

(7) This is a special case of the general three-component triangular kinetic system of first-order reactions covered by the Korvezee equations.[8]

(8) *Cf.* A. E. Korvezee, *Recl. Trav. Chim. Pays-Bas.*, **59**, 913 (1940).

Table I. Ratio of Rate Constants (k_d/k_i) for 2,3 Cleavage *vs.* Geometric Isomerization in Intermediates of the Type R$_1$R$_2$C–CH$_2$–CH$_2$–CR$_3$R$_4$

R$_1$	R$_2$	R$_3$	R$_4$	k_d/k_i	Temp, °C	Ref
H	CH$_3$	H	CH$_3$	4	401^j	a
H	CH$_3$	H	CH$_3$	8	401^k	a
H	CH$_3$	OH	CH$_3$	8	381^j	b
CD$_3$	CH$_3$	CD$_3$	CH$_3$	$\geqslant 22$	401	c
CH$_3$	C$_2$H$_5$	CH$_3$	C$_2$H$_5$	$\geqslant 48^{d,g}$	148^h	f
CH$_3$	C$_2$H$_5$	CH$_3$	C$_2$H$_5$	$\geqslant 64^{e,g}$	148^i	f

^{a} H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 4884 (1961). ^{b} E. D. Feit, *Tetrahedron Lett.*, 1475 (1970). ^{c} Present work. ^{d} Derived from the *meso*-azo compound. ^{e} Derived from the *d,l*-azo compound. ^{f} P. D. Bartlett and N. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968). ^{g} % olefin/<2% "crossover" cyclobutane in thermal reaction. ^{h} At room temperature, the photolytically generated singlet diradicals show k_d/k_i ∼12 and ∼20 from *meso*- and *d,l*-azo compounds, respectively. ^{i} From the *cis*-cyclobutane. ^{k} From the *trans*-cyclobutane.

the data as representative of the properties of a putative intermediate 1,4-butanediyl. Irreversible cleavage of the C$_2$–C$_3$ bond to produce olefin from this species is much faster than C$_1$–C$_2$ and C$_3$–C$_4$ bond rotation–recyclization. This behavior is in sharp contrast to that of the corresponding 1,3-propanediyl derived from tetramethylcyclopropane, in which the ratio of rates of irreversible intramolecular olefin-forming hydrogen transfer[9] and bond rotation–recyclization[5] at 401° is about four orders of magnitude smaller than the value k_d/k_i in the present case. The result is at least qualitatively concordant with the estimate[2a] of a substantially higher activation energy for hydrogen shift in 1,3-propanediyl than for 2,3-bond cleavage in 1,4-butanediyl, a bias that should be accentuated by the substitution in the tetramethyl cases.

Table I shows that the k_d/k_i ratio for a series of 1,4-butanediyls increases with increasing terminal substitution. The effect agrees with that expected of an increase in k_d because of increasing stability of the fragment olefins and of a decrease in k_i because of the more negative entropy of activation associated with more massive rotors.[10]

(9) (a) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3052 (1962); (b) C. Blumstein, D. Henfling, C. Sharts, and H. E. O'Neal, *Int. J. Chem. Kinet.*, in press.

(10) This ponderal entropy effect on the rotor has been predicted[2a] and is in qualitative agreement with intermolecular[5,11] and intramolecular[11] comparisons of cyclization *vs.* rotation in 1,3-propanediyls. An increased rotational barrier would operate in the same direction, but its importance relative to the ponderal entropy effect cannot be accurately evaluated at present.

(11) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7345 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

(12) Supported by Postdoctoral Fellowship No. 1 FO2 GM34,242-01 of the National Institute of General Medical Sciences.

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1,1′-Spirobibenzocyclobutene from an Allenic *o*-Quinomethane Intermediate

Sir:

The hitherto unreported hydrocarbon 1,1′-spirobibenzocyclobutene (**1**) is of interest not only as a particu-

larly strained benzocyclobutene, but also as the parent hydrocarbon of a diradical which is predicted to be appreciably stabilized by spiroconjugation.[1] We now report the first synthesis of **1**, by a process involving a

1　　　　　　　**2**
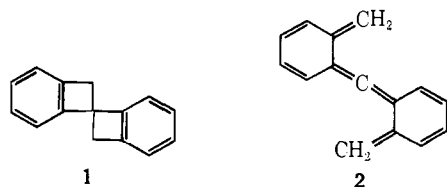
novel *o*-quinonoid allene (**2**), as well as several other transformations of the intermediate allene **2**.

Bromination of 2,2'-dimethylbenzophenone (**3**)[2] by *N*-bromosuccinimide (irradiation) in carbon tetrachloride gave (18%) the dibromide **4**,[3] mp 115–116°, which reacted with thiourea in ethanol to give (61%) the bisthiouronium salt **5**, mp 225–226°. Alkaline hydrolysis of **5**, followed by acidification, afforded (89%) the spirobisulfide **6**, mp 106–107°, which was oxidized quantitatively by peracetic acid to the spirobisulfone **7**, mp 288–289°. Gas-phase pyrolysis of **7** (10 mm N_2 pressure) over a glowing Nichrome coil[4] (700°) and trapping of the pyrolysate at −78° afforded a low yield (7%) of resublimable products, consisting mainly of a 2:1 mixture of hydrocarbon **1** and ketone **3**.

3, R = H
4, R = Br
5, R = $S(NH_2)_2{}^+Br^-$

6　　　　　　**7**
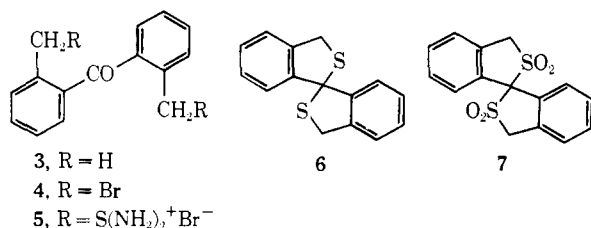
Hydrocarbon **1**, mp 69–70°, showed a molecular ion base peak at *m/e* 192, in accord with the composition $C_{15}H_{12}$. Its nmr spectrum showed only an aromatic multiplet around δ 7.2 and a benzylic singlet at 3.55 in the ratio of 2:1. Its uv spectrum in ethanol showed a typical benzocyclobutene chromophore: λ_{max} 262.5 mμ (log ε 3.44), 268.5 (3.59), and 274.5 (3.59).

From the pyrolysis tube walls immediately above the Nichrome coil was obtained, in 15% yield, a hydrocarbon $C_{30}H_{24}$, mp 243–244°, which was assigned the structure of 5,11-di-*o*-tolyldibenzo[*a,e*]cyclooctatetraene (**8**) on the basis of mechanistic considerations, its stability at 300°, and spectral evidence. Thus, the uv spectrum of **8** in ethanol showed no maxima, but only a shoulder at 235 mμ (log ε 4.20). Its nmr spectrum showed only a methyl singlet at δ 2.23 and an aromatic multiplet centered at 7.15 in a ratio of 1:3. Its mass spectrum showed, in addition to the molecular ion at *m/e* 384, peaks at *m/e* 293, 202, and 268 corresponding to the loss of one tolyl (C_7H_7), two tolyls ($2C_7H_7$), and a tolylacetylene unit (C_9H_8), respectively. Confirmation of

the structure of **8** was obtained by an independent synthesis of the hydrocarbon from *o*-benzenediazonium carboxylate and *o*-tolylacetylene, following the general procedure reported for the synthesis of the *p*-tolyl analog of **8** from *p*-tolylacetylene.[5]

8　　　　　**9**　　　　　**10**
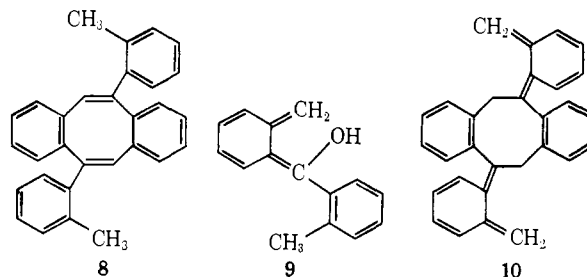
The unusual allenic intermediate **2** can serve as precursor for products **1**, **3**, and **8** from the pyrolysis of spirobisulfone **7**. Thus, intramolecular cyclization of **2** gives **1**, addition of water to **2** yields enol **9** which tautomerizes to **3**,[6] and a nonconcerted 4 + 4 dimerization of **2** gives dimer **10**, which rearranges by two 1,5-hydrogen shifts[7] to **8**.

More practical routes to **1** and its derivatives are being sought in our laboratory.

(5) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964).
(6) The addition of water to a reactive isoindene derivative has been reported: K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).
(7) The analogous thermal rearrangement of α,α'-dimethyl-*o*-quinodimethane to *o*-ethylstyrene has been observed: M. P. Cava and M. J. Mitchell, *Rev. Chim. Acad. Repub. Pop. Roum.*, **7**, 737 (1962).
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Mechanism of Olefin Formation in the Reaction of Carbethoxycarbene with Alkyl Halides[1]

Sir:

There are widely scattered and isolated reports in the chemical literature of formally similar reactions in which a compound R–X reacts with carbethoxycarbene to produce an olefin and/or XCH_2COOEt (*e.g.*, X = OR,[2] –Cl,[3] –Br,[3] and –NR_2[4]). This reaction pathway gen-

(1) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF Grant No. 1035-G1 and 4469-AC4), for partial support of this work.
(2) (a) J. R. Bartels-Keith, A. W. Johnson, and W. I. Taylor, *J. Chem. Soc.*, 2352 (1951); (b) J. R. Bartels-Keith, A. W. Johnson, and A. Langemann, *ibid.*, 4461 (1952); (c) R. B. Johns, A. W. Johnson, and J. Murray, *ibid.*, 198 (1954); (d) G. B. R. de Graaf, J. H. van Dijk-Rothuis, and G. van de Kolk, *Recl. Trav. Chim. Pays-Bas*, **74**, 143 (1955); (e) G. B. R. de Graaf and G. van de Kolk, *ibid.*, **77**, 224 (1958); (f) A. W. Johnson, A. Langemann, and J. Murray, *J. Chem. Soc.*, 2136 (1953); (g) V. Franzen and L. Fikentscher, *Justus Liebigs Ann. Chem.*, **617**, 1 (1958).
(3) (a) V. Franzen, *ibid.*, **627**, 22 (1959); (b) I. A. Dyakonov and T. V. Domareva, *Zh. Obshch. Khim.*, **25**, 1486 (1955); (c) I. A. Dyakonov and N. B. Vinogradova, *ibid.*, **22**, 1349 (1952); (d) I. A. Dyakonov and N. B. Lugovtsova, *ibid.*, **21**, 839 (1951); (e) I. A. Dyakonov and N. B. Vinogradova, *ibid.*, **23**, 66 (1953); (f) I. A. Dyakonov and N. B. Vinogradova, *ibid.*, **29**, 3099 (1959); (g) D. D. Phillips, *J. Amer. Chem. Soc.*, **76**, 5385 (1954); (h) W. H. Urry and J. W. Wilt, *ibid.*, **76**, 2594 (1954); (i) J. W. Wilt, Ph.D. Thesis, University of Chicago, 1954.

(1) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967).
(2) M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1542 (1941).
(3) New compounds were characterized by consistent spectral properties, including mass spectra, and by elemental analysis.
(4) For some other examples of the synthesis of condensed cyclobutane aromatic systems by sulfone pyrolyses, see the following: (a) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959); (b) M. P. Cava, A. A. Deana, and K. Muth, *ibid.*, **82**, 2524 (1960); (c) M. P. Cava and R. L. Shirley, *ibid.*, **82**, 654 (1960); (d) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).