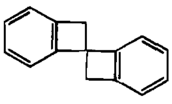
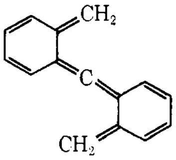
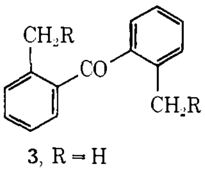
larly strained benzocyclobutene, but also as the parent hydrocarbon of a diradical which is predicted to be appreciably stabilized by spiroconjugation.[1] We now report the first synthesis of **1**, by a process involving a novel *o*-quinonoid allene (**2**), as well as several other transformations of the intermediate allene **2**.

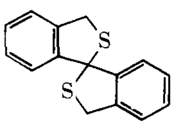

1


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 = $S(NH_2)_2^+Br^-$



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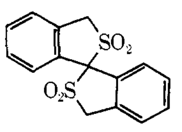
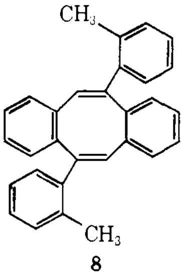


7

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]



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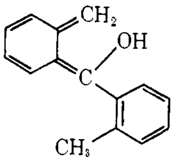

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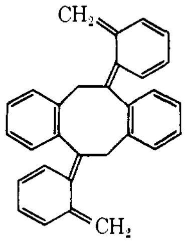

10

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.

Acknowledgment. We thank the National Science Foundation for generous support of this research.

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(2) M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1542 (1941).

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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.

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(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.

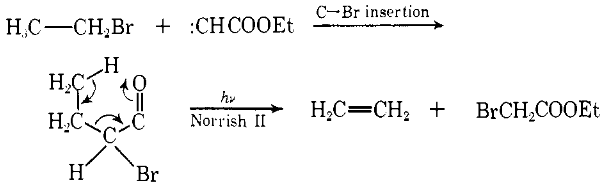
erally competes poorly with other modes of reaction such as insertion into carbon–hydrogen bonds and addition to carbon–carbon double bonds. Hitherto, no detailed mechanistic study has appeared to account for the formation of elimination products in these reactions. We now report the results of such a study undertaken for the reaction of carbethoxycarbene with alkyl halides.

Solutions of ethyl diazoacetate[5] in an excess of the alkyl halide studied were irradiated at 10 ± 1° with a 200-W Hanovia medium-pressure mercury arc lamp fitted with a Pyrex shield. A series of alkyl halides, RX (R = Et, *i*-Pr, *sec*-Bu, *tert*-Bu; X = Cl, Br, I), was studied. In all cases, the yield of olefin (determined as per cent yield of XCH_2COOEt) fell in the range 30–41%. When competition reactions were run using equimolar mixtures of alkyl halides RCl + RBr + RI all bearing the same alkyl residue, R–, selectivity was demonstrated by the carbene in its reaction with C–X bonds: the reactivity ratio X = Cl:Br:I = 1.0:1.5:2.2 was observed.

No carbene dimers (diethyl maleate or fumarate) and only traces of products arising from carbon–halogen bond insertion could be detected. However, a viscous oil remained as residue when the volatile products were removed by distillation. This oil is probably a mixture of self-condensation products, some being of the type analogous to those previously reported[6] to be formed when methyl diazoacetate is photolyzed in benzene solution.

Ethyl bromide was chosen as substrate in an effort to delineate the mechanism of the reaction of carbethoxycarbene with alkyl halides. For this reaction, the rates of nitrogen evolution and ethylene formation were found to be identical within experimental error ($k_1 = 4 \times 10^{-3}$ min^{-1} at 10 ± 1°), suggesting that the rate-determining step is the initial photodecomposition of the ethyl diazoacetate.

One possible explanation for the formation of ethylene is that it arises *via* a secondary photochemical (Norrish type II) process involving the carbon–bromine bond insertion product, ethyl α-bromobutyrate, as intermediate.[7] However, this possibility was readily excluded. It has been shown that ethyl α-bromobutyrate photolyzed in the presence of ethyl bromide or in benzene solution fails to form ethyl bromoacetate or ethylene. Furthermore, the addition of ethyl α-bromobutyrate to a solution of ethyl bromide plus ethyl diazoacetate followed by subsequent irradiation results in no increase in the total amounts of ethylbromoacetate and ethylene produced. This latter study also rules out the possibility of any contribution from the hypothetical reaction Et—CHBr—COOEt + N_2CH-COOEt → $H_3C—CH{=}CHCOOEt$ + $BrCH_2COOEt$, an analogy of which has been proposed to account for XCH_2COOEt among the products of reactions of carbethoxycarbenoid with some monohalogenated substrates.[3e,8] Further control studies indicated that no direct photoelimination on ethyl bromide was occurring under the conditions employed in our study.



Of the several mechanistic alternatives involving primary reaction of the carbene with ethyl bromide, one involving α elimination was tested experimentally.

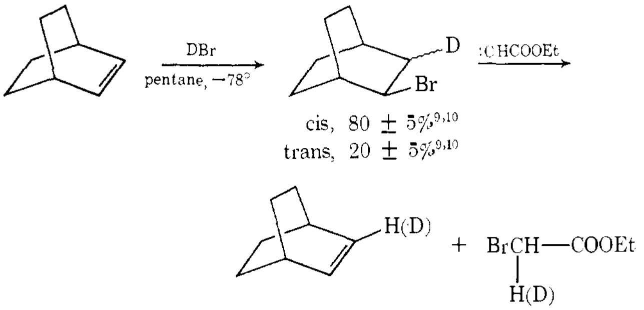
$$Y_3C—CH_2Br + :CHCOOEt \longrightarrow$$

$$BrCH_2COOEt + Y_3C—\ddot{C}H \xrightarrow{\sim Y:} Y_2C{=}CHY$$

Y = H or D

Mass spectral analysis of both the ethylene and the ethyl bromoacetate produced from reaction of the carbene with β,β,β-trideuterioethyl bromide revealed *no trace* of ethylene-d_3 or of ethyl bromoacetate-d_0, the sole products being the -d_2 and -d_1 compounds, respectively. We can therefore conclude that ethylene and ethyl bromoacetate are produced exclusively by β elimination of HBr from ethyl bromide in this reaction.

The stereochemistry of the elimination was examined using 3-deuterio-2-bromobicyclo[2.2.2]octane. Symmetry considerations require that the stereochemistry of the elimination not be prejudiced by geometrical factors in the product olefin. Mass spectral analysis of the bicyclo[2.2.2]octene thus produced reveals that the elimination proceeds with 80% cis stereoselectivity.[10] In contrast, we find that the corresponding E2 elimination performed in KO-*tert*-Bu–*tert*-BuOH is 26% stereoselective cis.[10]



The above observations are consistent with a stepwise mechanism for the elimination involving the carbene. This conclusion derives additional support from our observation that mixtures of $D_3C–CH_2Br$ and $H_3C–CH_2Br$ of accurately known isotopic composition (mass spectral) when reacting competitively with carbethoxycarbene afford ethylene and ethyl bromoacetate whose deuterium contents both reflect *no* primary deuterium isotope effect on the isotopic composition of the products ($k_H/k_D = 1.00 \pm 0.05$).[11]

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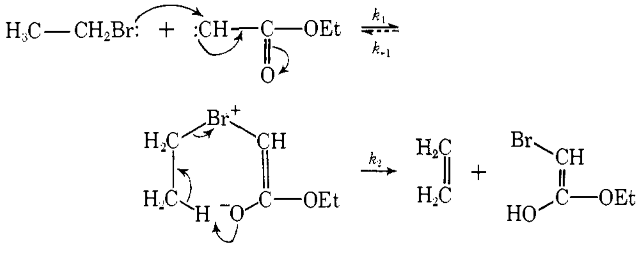
(9) N. M. Brockway and A. P. Marchand, Abstracts, 25th Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec 4–6, 1969, No. 19.

(10) Vpc analysis of the olefin produced in the reaction of carbethoxycarbene with 3-deuterio-2-bromobicyclo[2.2.2]octane revealed the presence of a small amount of bicyclo[3.2.1]oct-2-ene. We are actively seeking the source of this material, *i.e.*, whether it arises *via* competing Wagner–Meerwein rearrangement which occurs during the addition of DBr to bicyclo[2.2.2]octene, or, alternatively, if it is formed during the subsequent elimination step involving the carbene. The numbers given indicating the stereoselectivity of the addition and elimination reactions are therefore approximate. A full quantitative analysis of our results will be given in the full paper.

We envision the mechanism of the elimination reaction as involving the formation of an intermediate bromonium ylide.[12] If the ylide once formed does not



often regenerate carbene (*i.e.*, $k_2 \gg k_{-1}$), then within the limits of applicability of the steady-state approximation we would expect to see *no* primary kinetic isotope effect, as is indeed the case. In terms of the above mechansim, the observed absence of a primary kinetic isotope effect requires that k_1 (or the sequence of reactions represented by k_1) be rate determining. The observed stereoselectivity (but not stereospecificity) of the elimination reaction suggests a further breakdown of the ylide, perhaps to a diradical intermediate which can then collapse rapidly to give predominantly but not exclusively cis elimination product.[13]

We have extended our study to include the reaction between neopentyl bromide (no β hydrogens) and carbethoxycarbene. Here, direct carbon–hydrogen or carbon–bromine bond insertion might occur. Alternatively, abstraction of bromide ion by the carbene might occur, followed by rearrangement to a tertiary carbonium ion which might then either eliminate to form olefin or recombine with the $\text{BrC}^{-}\text{HCOOEt}$ moiety to give a "rearranged insertion product" (ethyl 2-bromo-3,3-dimethylvalerate). In our hands, the reaction gave only unrearranged insertion products; the C–Br bond insertion product (ethyl 2-bromo-4,4-dimethylvalerate) predominated over that arising *via* primary C–H bond insertion (ethyl 3,3-dimethyl-4-bromovalerate) by a factor of *4*, despite the 9:1 statistical predominance of primary C–H bonds in the substrate!

In view of the observed predisposition of the carbene to insert into the C–Br bond in neopentyl bromide, we are currently examining the reaction of carbethoxycarbene with other suitably substituted alkyl halides which cannot directly react *via* β elimination with an eye toward the possible synthetic utility of this reaction. We shall communicate the results of our study shortly.

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(11) Mass spectral deuterium analyses were performed in the laboratory of Mr. Seymour Meyerson, American Oil Co., Whiting Ind. We thank Mr. Meyerson for rendering his facilities and guidance in this connection.

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(13) We gratefully acknowledge the suggestions of a referee, which are embodied in our formulation of the elimination reaction mechanism.

(14) National Aeronautics and Space Administration Predoctoral Trainee, 1965–1968.

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Orbital Symmetry Control in the Photochemistry of 1,3,5-Hexatrienes

Sir:

The photoisomerization of a 1,3,5-hexatriene to a bicyclo[3.1.0]hex-2-ene is a well-documented photoreaction.[1–13] If concerted, this intramolecular photo-Diels–Alder reaction can be viewed as a 4 + 2 cycloaddition, in which case it should be either a $(\pi^{4}\text{s} + \pi^{2}\text{a})$ or a $(\pi^{4}\text{a} + \pi^{2}\text{s})$ process.[14] Alternatively, it could be viewed as a 2 + 2 + 2 cycloaddition which would be photochemically allowed if antarafacial on all three components or on one. It is interesting to note that, in the few cases where the hexatriene is sufficiently labeled to provide a test of these conclusions,[1c,10–12] the gross observations made are not in accord with orbital symmetry predictions. In the hope of providing some data for understanding the stereochemical course of this reaction, we have investigated the photochemistry of a series of 1,2,6-triphenyl-1,3,5-hexatrienes. The result of our studies appears to be compatible with the theoretical predictions.

1,2,6-Triphenyl-(*Z*,*Z*,*E*)-hexa-1,3,5-triene[15] (**1**; mp 78–80°), prepared by the Wittig reaction of triphenyl-*trans*-cinnamylphosphonium bromide and *cis*-2,3-diphenylacrolein,[16] upon irradiation[17] rearranges stereospecifically to give an isomeric species (76%; mp 104–106°) to which we have assigned the structure of *exo*,*exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**2**).[18] The stereochemical assignment was based on the following nmr (CCl_4) data: δ 1.71 (t, 1, C_6H), 2.02 (dd, 1, C_5H), 2.31 (m, 1, C_1H), 4.41 (t, 1, C_4H), 6.80 (t, 1, C_2H), and 7.25 (m, 15, aromatic). Appropriate spin-decoupling experiments were performed which allowed

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