Reactions of Diphenylcarbene with Alkenes, Alkynes, and Alkenynes[1,2]

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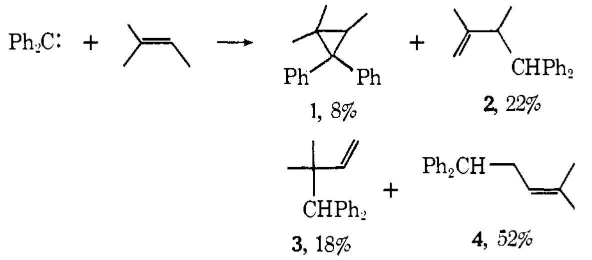
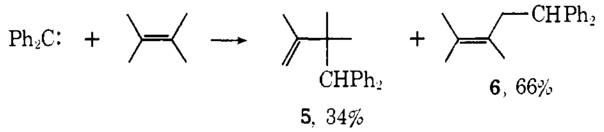
Abstract: Diphenylcarbene reacts with olefins by both addition and abstraction. The partitioning of the reaction between these paths is determined largely by steric factors. The stereochemistry of addition has been determined in a system favorable to triplet reaction. With acetylenes, both addition and abstraction occur, but the intermediate generated by addition is often diverted from a path leading to the usual cyclopropene and gives indene instead. Addition to dimethylacetylene gives the conventional cyclopropene, but more highly substituted alkynes react exclusively through hydrogen abstraction. Again steric factors are considered reponsible. Enynes are subject to the same effects, although when addition does occur, the double bond is favored.

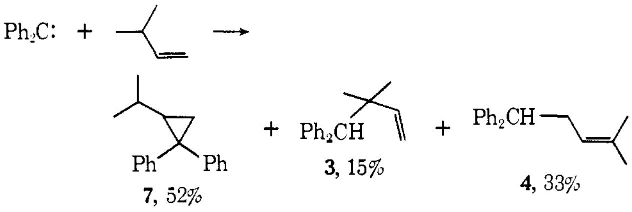
In 1959, Etter, Skovronek, and Skell[5] described the reaction of diphenylcarbene (DPC) with *cis*- and *trans*-2-butene. The later reports of Closs and Closs[6–8] and Humer[9] which refined the early misleading results revealed DPC to be a species that reacts with the 2-butenes largely by hydrogen abstraction and subsequent recombination of the radicals produced. This may seem curious, as most triplets react with olefins by addition, not abstraction.[10,11] DPC, the first triplet to have its properties described, has come to be regarded as the archetype of the species. As the initial description of this species was in error[5] and as we had been puzzled by the abstraction reactions of DPC for some years, we undertook a study of the reactions with many π sytems in the hopes of clarifying the situation.

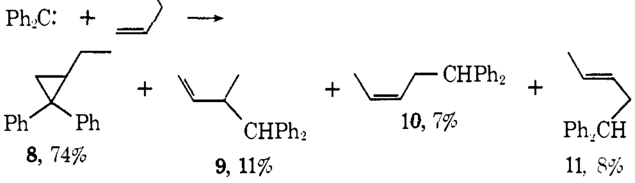
We find the reaction of DPC with the 2-butenes to be much as previously described[6–9] although we observe slightly more addition. More highly substituted olefins give even greater percentages of abstraction-recombination. Thus, 2-methyl-2-butene gives **1–4** and 2,3-dimethyl-2-butene gives **5** and **6** on reaction with DPC.[12] Others[13–15] have generated DPC through the photoinduced fragmentation of cyclopropanes and oxiranes, and here only the products of radical dimerization were reported.

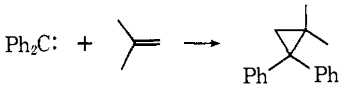




Less substituted olefins behave differently, however, and here cyclopropanes predominate. With isobutene and propene we can find *only* the corresponding cyclopropanes (**12** and **13**, respectively).







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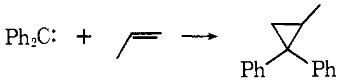

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(1) Support of this work by the National Science Foundation through Grants GP-12759 and GP-30797X is gratefully acknowledged.

(2) Portions of this work are taken from the Ph.D. Theses of W. J. B. and M. E. H., Princeton University, 1972 and 1971, respectively. Smaller sections have been the subject of prior communication: (a) M. Jones, Jr., W. J. Baron, and Y. H. Shen, *J. Amer. Chem. Soc.*, **92**, 4745 (1970); (b) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *ibid.*, **93**, 1554 (1971).

(3) National Science Foundation Trainee, 1971–1972.

(4) National Science Foundation Predoctoral Fellow, 1967–1971.

(5) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Amer. Chem. Soc.*, **81**, 1008 (1959).

(6) G. L. Closs and L. E. Closs, *Angew. Chem., Int. Ed. Engl.*, **1**, 334 (1968).

(7) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

(8) See also unpublished work of G. L. Closs reported in R. A. Moss and U.-H. Dolling, *J. Amer. Chem. Soc.*, **93**, 954 (1971).

(9) P. W. Humer, Ph.D. Thesis, Pennsylvania State University, University Park, Pa., 1964.

(10) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(11) M. Jones, Jr., and R. A. Moss, Ed., "Carbenes," Interscience, New York, N. Y., 1973.

(12) All new compounds encountered in this work were characterized by combustion or mass spectral analysis and examination of spectra. These spectra can be found in Tables III and IV in the Experimental Section. Control experiments (see Experimental Section) demonstrated that the hydrocarbon mixtures were unaffected by the irradiation conditions. The thermal stability of the products was checked by reinjection into the gas chromatograph. No isomerization was found.

(13) H. Kristinsson, K. N. Mehrotka, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (*London*), 1562 (1966).

(14) P. Petrellis and G. W. Griffin, *Chem. Commun.*, 691 (1967).

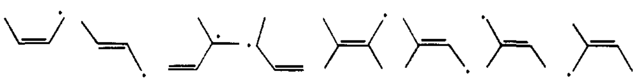
(15) T. I. Temnikova and I. P. Stapanov, *Zh. Org. Khim.*, **2**, 1525 (1966).

Thus it is very clear that the mode of reaction of DPC with olefins depends intimately upon the substitution of the olefin. The abstraction reaction noted with the 2-butenes is not an inherent property of triplet DPC, but rather depends upon the reaction partner as well (Table I).

Table I. Mode of Reaction of Diphenylcarbene with Olefins

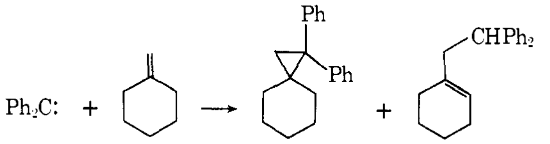
Olefin	% cyclopropane	% abstraction–recombination
Propylene	100	0
Isobutylene	100	0
Methylenecyclohexane	87	13
1-Butene	74	26
3-Methyl-1-butene	52	48
trans-2-Butene	22	78
2-Methyl-2-butene	8	92
2,3-Dimethyl-2-butene	0	100

We see two possible explanations for this dependence and can give evidence that one of them is dominating. In the reactions giving substantial abstraction the radicals so formed are all stabilized by one or more alkyl groups. There is a general trend for the most highly substituted olefins to give the most abstraction. The two examples of exclusive addition would yield



radicals without such stabilization. An initial case might be made that this electronic effect was a prime

cause of the abstraction shown by DPC in many systems. However, one might ask why other carbenes do not abstract from these olefins. Moreover there are other inconsistencies. 1-Butene, for instance, would give the same radical as 2-butene, and the amount of abstraction is much greater from the 2-butenes. Similarly, methylenecyclohexane gives **14** and **15** in the ratio 87:13, and clearly does not favor



14, 87% **15**, 13%

abstraction as it should if radical stability were the important factor.

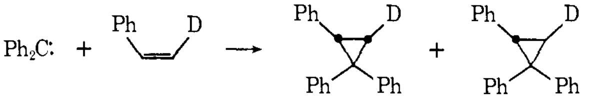
We feel that steric factors must be paramount in the control of the reaction path. The more alkyl groups present, the more shielding of the double bond and the more reaction at the periphery of the molecule.

We might compare DPC with fluorenylidene, a related carbene that reacts primarily by addition in every case so far examined.[16,17] However, fluorenylidene is necessarily flat and DPC is free to adopt a nonplanar structure. If this were to be the case, steric difficulties experienced by DPC would be more understandable. The most recent spectroscopic studies of triplet DPC implicate a bent, twisted structure, at least in rigid medium.[20,21] We suggest that a similar structure probably applies in solution.

It seems a fair assumption that the products of abstraction are due to triplet DPC, as it is clear from the structures of the products that allylic radicals are involved. Direct insertion cannot account for the major amount of the products although we cannot exclude a minor contribution. CIDNP experiments by Closs and Trifunac[22] implicate triplet DPC in the abstraction reaction from toluene.

The data also allow some comment upon the spin state leading to the cyclopropanes. The compounds formed from *cis*-2-butene are produced in a largely stereospecific fashion.[6–8] Closs reports that *cis*-2-butene gives a cis:trans ratio of either 87:13[6] or 77:23[3] and that *trans*-2-butene gives a trans:cis ratio of 96:4.[6] Thus they must be formed mainly from the singlet state, while the triplet is the source of the olefins. There is a growing conviction that singlet and triplet DPC are in equilibrium,[7] and thus the discovery of reactions of both spin states occurring at the same time is no real surprise. As cycloaddition forms only a small portion of the products from *cis*-2-butene and as the carbene apparently has difficulty in penetrating to the π bond, it seemed of interest to determine the stereochemistry of addition in a system free from abstraction. Propene or styrene would be an apt substrate, and we have examined the latter.

cis-β-Deuteriostyrene was prepared according to the literature,[23,24] and allowed to react with DPC. The structures and stereochemistry of the products (*cis*- and *trans*-**16**) were determined by nmr spectroscopy. In cyclopropyl compounds vicinal coupling constants have been measured and found to lie within the limits J_{cis} = 6.6–12.5 Hz and J_{trans} = 3.9–8.6 Hz. In every case J_{cis} was larger than J_{trans}.[25] We find two doublets in the upfield portion of the nmr spectrum of the cyclopropanes formed from DPC and *cis*-β-deuteriostyrene. The higher field doublet (J = 9 Hz) was assigned to the cis cyclopropane and the lower field doublet (J = 6.5 Hz) to the trans. Integration of the signals showed that reaction in neat styrene led to 65% cis addition and 35% trans. If we make the assumption that triplet DPC would give equal amounts of cis and trans products, the observed ratio corresponds to a reacting mixture of 70% triplet and 30% singlet. Of course such an analysis also



cis-**16**, 65% *trans*-**16**, 35%

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(16) M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4013, 4015 (1965).

(17) It has been implied that fluorenylidene reacts with cyclohexene by abstraction.[18] However, the product of addition is formed in at least equal amount.[19]

(18) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1512 (1971).

(19) M. Jones, Jr., Ph.D. Thesis, Yale University, New Haven, Conn., 1963.

(20) C. A. Hutchison, Jr., and B. E. Kohler, *J. Chem. Phys.*, **51**, 3327 (1969).

(21) D. C. Doetschman and C. A. Hutchison, Jr., *ibid.*, **56**, 3964 (1972).

(22) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2186 (1970).

(23) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970).

(24) A. Hossner, F. P. Boerwinkle, and A. B. Levy, *ibid.*, **92**, 4879 (1970).

(25) S. Sternhill, *Quart. Rev., Chem. Soc.*, **23**, 248 (1969).

supposes that the singlet and triplet react with styrene at the same rate and this cannot be the case. Indeed styrene should be an especially good triplet trap,[26] and the above 70:30 ratio reflects the reacting mixture in a system very favorable to triplet addition. In other cases the singlet should be more important. Obviously, in systems in which triplet abstraction is the primary reaction, the cyclopropanes will be formed largely from the singlet. This appears to be the case with the 2-butenes.

The cis:trans cyclopropane ratio can be affected by addition of hexafluorobenzene, a molecule inert to DPC. Added hexafluorobenzene slightly increases the amount of trans adduct as shown in Table II.

Table II. Stereochemistry of Addition to Styrene as a Function of Added Hexafluorobenzene

Mol % of hexafluorobenzene	% cis adduct	% trans adduct
0	65	35
36	60	40
50	59	41
80	56	44
90	55	45
95	56	44

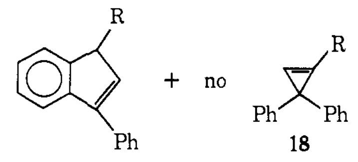
At 80–95% hexafluorobenzene there can be no more than 12% singlet reacting. Presumably unreactive collisions allow DPC to approach equilibrium more closely and the ground-state triplet[20,21] is naturally favored.

Control experiments demonstrated that neither the products nor the styrene was isomerized under the reaction conditions. Further, the pyrazolines which would lead to the observed adducts were not decomposed by the light sources used.

Triplet DPC reacts with olefins in two ways: addition and abstraction, and each of the reactions is a two-step process. The same is true of alkynes. Here, of course, there is no stereochemical label to reveal the stepwise nature of the addition reaction. We felt that any addition must be stepwise and hoped that an intermediate diradical could be trapped by one of the benzene rings of DPC. This hope was realized in the reactions with monosubstituted acetylenes, as the indenes **17a–c** are the sole products of the addition of DPC to the alkynes shown. The conventional[10,11] cyclopropenes (**18a–c**) are missing. Before the mechanism of indene formation is discussed, it must first be shown that the indenes are primary products and not formed by subsequent isomerization of cyclopropenes. Such a process is not without precedent. Both thermal[27–29] and photochemical[27,30–35] rearrangements are known. However, the thermal reaction requires high temperatures not encountered in the reactions we have described. For instance, 3-phenylindene is formed from 3,3-diphenylcyclopropene at 200° in a gas chromatograph,[27] and such conditions were not approached. It is less easy to discount photochemical processes. The needed sample of 3,3-diphenyl-1-methylcyclopropene (**18a**) was obtained through irradiation of 3,3-diphenyl-5-methyl-3*H*-pyrazole, itself formed by allowing diphenyldiazomethane and methylacetylene to stand together in the dark for 5 weeks. The cyclopropene **18a** was accompanied by indene **17a** and the ratio of these products (2:1) served to eliminate the pyrazole as a source of **17** in the reaction of DPC with acetylenes. Similarly, both the benzophenone- and diphenyldiazomethane-sensitized decompositions of the pyrazole gave substantial amounts of **18a**. Finally, neither direct nor benzophenone-sensitized irradiation of pure **18a** led to **17a**. Exactly analogous experiments were performed with the pyrazoline formed from *tert*-butylacetylene and diphenyldiazomethane.

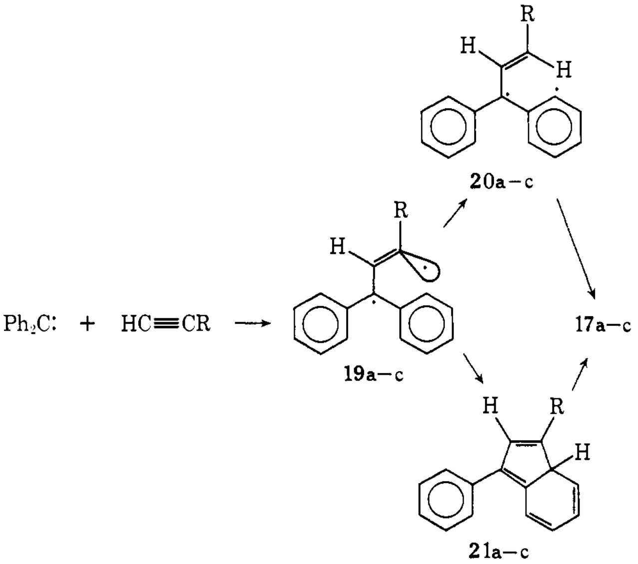
$Ph_2C: + R—C{\equiv}CH \longrightarrow$

a, $R = CH_3$
b, $R = (CH_3)_3C$
c, $R = Ph$



17 **18**

The gross mechanism proposed for the formation of **17** begins with the addition of DPC to the less substituted end of the acetylenes to generate **19a–c**. This intermediate may or may not be initially the triplet carbene shown, but in any event it should quickly relax to such a structure. Several routes are open for further progress toward **17**. One involves abstraction of an ortho hydrogen followed by closure of the new diradical **20**. Another proceeds through addition to the ring to give **21** and subsequent 1,5-hydrogen shift



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[26] R. A. Moss, "The Application of Relative Reactivity Studies to the Carbene Olefin Addition Reaction," in ref 11.

[27] G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969).

[28] J. A. Walker and M. Orchin, *Chem. Commun.*, 1239 (1968).

[29] M. A. Battiste, B. Halton, and R. M. Grubs, *ibid.*, 907 (1967).

[30] B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971).

[31] L. Schrader, *Chem. Ber.*, **104**, 941 (1971).

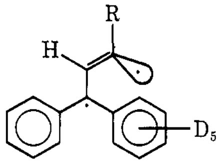
[32] H. Dürr and L. Schrader, *ibid.*, **103**, 1334 (1970).

[33] H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966).

[34] H. Dürr, *Justus Liebigs Ann. Chem.*, **723**, 102 (1969).

[35] H. Dürr, *Chem. Ber.*, **103**, 369 (1970).

to rearomatize to **17**. A third possibility features insertion into the ortho carbon–hydrogen bond to give **17** directly. This last reaction should be possible only for a singlet and is therefore less likely than the other two. In order to differentiate these possibilities, we have measured the deuterium isotope effect on the reaction by forcing an internal competition in **19**. Use of DPC-d_5 should yield **22**, a variant of **19**, in which the choice of hydrogen or deuterium will either result in an observable isotope effect or not, depending upon the mechanism. A primary isotope effect would be expected if either abstraction or insertion were involved in the mechanism. A value of $k_H/k_D = 1.55$ has been given for the insertion of singlet methylene into the vinylic carbon–hydrogen bond of *cis*-2-butene.[36] The intramolecular insertion of *o*-*n*-butylphenylcarbene to give 2-ethylindene showed a $k_H/k_D = 3.1–3.4$.[37] Thus an insertion reaction should show a substantial isotope effect. It is difficult to find precise analogy for a mechanism involving abstraction of an ortho hydrogen by a triplet carbene. Triplet methylene shows a k_H/k_D of *ca.* 3.9 for abstraction of the primary hydrogen of propane.[38] Substantial isotope effects are known in several intermolecular abstraction reactions.[39] Thus a mechanism in which hydrogen is abstracted from the ortho position should show $k_H/k_D > 1$.



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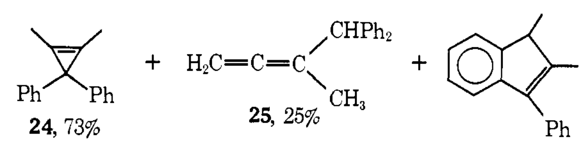
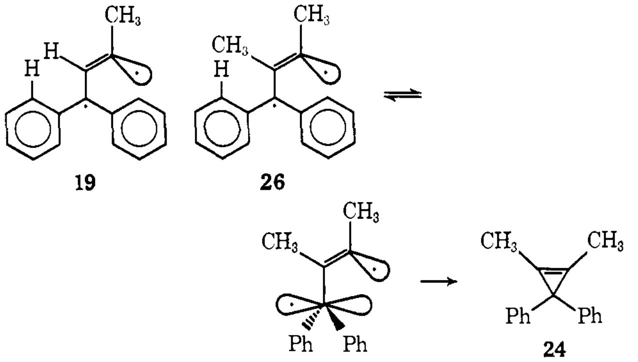
However, if addition to the ring were involved, one would expect only a small secondary isotope effect. We find no detectable isotope effect for the reaction with methyl- or *tert*-butylacetylene, and thus the mechanism proceeding through **21** obtains.[40]

The reaction of DPC with disubstituted acetylenes takes an entirely different course. Dimethylacetylene gives only 2% of the indene **23**. The main products are the cyclopropene **24** and the allene **25**.[12] Compound **25** is likely the product of hydrogen abstraction and its formation probably reflects the unavailability of an unsubstituted end of the acetylene for attack by DPC. However, both **23** and **24** are formed through addition of DPC to the acetylene to give **26**. The contrast with the reaction with methylacetylene, which gave only indene, is obvious. One must thus deal with a remarkable effect of the added methyl group. It appears to us that a new steric effect must be operating. The most obvious difference between **26** and **19** involves the methyl–hydrogen interaction indicated in **26**. Neither **19** nor **26** is a good cyclopropene source, as the orbitals which must be joined are orthogonal. However, should the methyl-hydrogen interaction induce rotation about the newly formed carbon–carbon bond, an excellent cyclopropene generator, here shown in extreme form as **27**, is produced.[41] To be sure, such a rotation can occur only at the cost of loss of allylic resonance, but the electron in the lone p orbital is well delocalized over the two phenyl rings and quite probably complete rotation to **27** is not necessary for formation of a species able to give cyclopropene.

$Ph_2C\colon + CH_3C{\equiv}CCH_3 \longrightarrow$

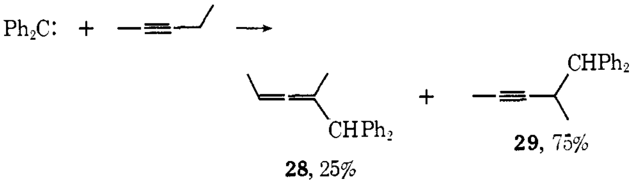


24, 73% **25**, 25% **23**, 2%

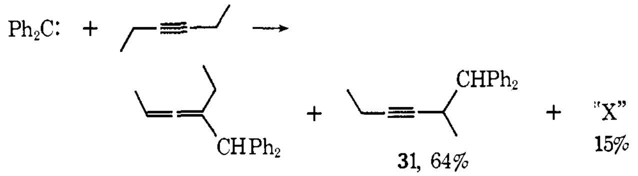


19 **26** **27** **24**

Elaboration of the substitution pattern to methylethylacetylene and diethylacetylene effectively halts addition to the triple bond. Neither cyclopropenes nor indenes are formed. The products (**28–31**) are most easily rationalized through an abstraction–recombination mechanism. Presumably here we see the same kind of steric effect postulated previously to account for the increase in abstraction as the substitution of alkenes increases. Also, in this case a secondary propargyl radical is formed, and this effect may contribute to the increased abstraction.



28, 25% **29**, 75%



30, 21% **31**, 64% "X" 15%

In addition to the usual spectral analysis,[12] compounds **28** and **29** were hydrogenated to 1,1-diphenyl-2-methylpentane which was compared to an authenic sample. Compounds **30** and **31** were identified by spectral analysis with special attention paid to com-

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(36) D. F. Ring and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **88**, 4285 (1966).

(37) T. A. Baer and C. D. Gutsche, *ibid.*, **93**, 5180 (1971).

(38) D. F. Ring and B. S. Rabinovitch, *Can. J. Chem.*, **46**, 2435 (1968).

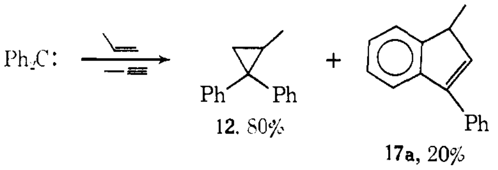
(39) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(40) Other intramolecular additions of radicals are known to go through addition mechanisms: D. H. Hay, *Advan. Free-Radical Chem.*, **2**, 47 (1967).

(41) The racemization of 1,3-diethylcyclopropene has recently been described in terms of rotation in a vinylcarbene: E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 2882 (1972).

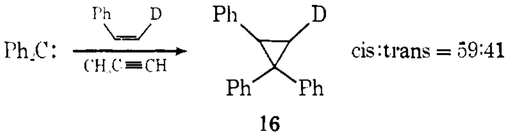
parisons with **28** and **29**. They were accompanied by 15% of an unidentified compound which, although it defied identification, was certainly neither cyclopropene nor indene.

We have also studied both inter- and intramolecular competitions between alkenes and alkynes. Intermolecular competitions establish that for the mixture of spin states available from direct irradiation of diphenyldiazomethane the double bond of propene is four times as reactive as the triple bond of methylacetylene. In an attempt to supplement this rather uninformative experiment, substrates better suited to reaction with triplet DPC were used. A competition between *cis*-β-deuteriostyrene and methylacetylene gave the product of addition to styrene (**16**) and only traces of **17a**. This is reasonable, as styrene is a much better triplet trap than is propene. Phenylacetylene competes more successfully for DPC, as 25% of the products in a competition reaction with styrene are derived from addition to the acetylene. In all cases, though, the alkene is more reactive than the acetylene.



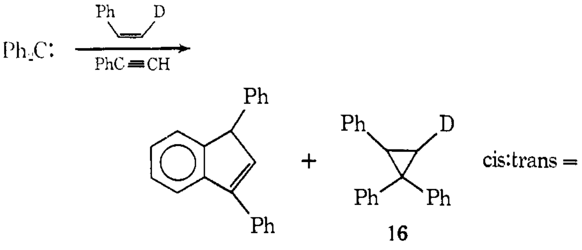
12, 80%

17a, 20%



cis:trans = 59:41

16



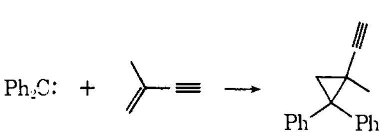
cis:trans = 60:40

17c

16

Three enynes were chosen for the intramolecular competitions. Very little data are available for such reactions. A single page in ref 10 suffices to describe all work done prior to 1971. What little has been reported has largely involved dichlorocarbene or the species formed on copper-catalyzed decomposition of ethyl diazoacetate. These electrophilic species prefer the ene part of the substrate to the yne, often to the exclusion of reaction at the triple bond.[42-44] The reaction of DPC with conjugated dienes to give exclusive 1,2 addition has recently been described.[45]

We find that DPC reacts only with the double bond of 2-methyl-1-buten-3-yne to give exclusively **32**. Neither cyclopropene nor indene could be found, and products of hydrogen abstraction were unimportant. Here we have a competition between unencumbered double and triple bonds. Not surprisingly, in view of the results of the intermolecular competition, the double bond wins out easily. In addition, reaction with the double bond yields an intermediate radical that is not only tertiary, but delocalized as well.



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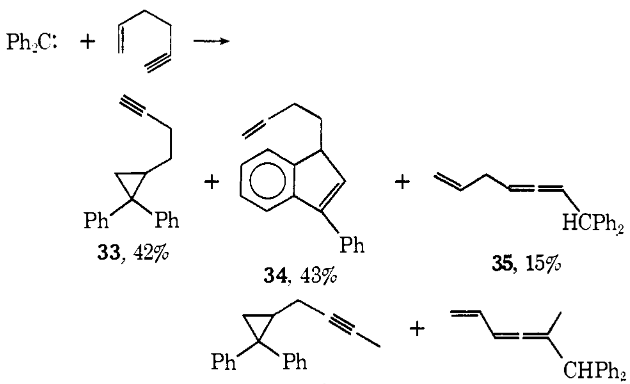
If the double bond is hindered with a more elaborate side chain, substantial reaction at the triple bond can be achieved. Thus, hex-1-en-5-yne gives, in addition to 42% cyclopropane (**33**), 43% indene (**34**) and 15% of a product derived from hydrogen abstraction (**35**). Interestingly, abstraction occurs from the position α to the triple bond. Perhaps interference with a vinyl hydrogen is avoided.

Finally, with hex-1-en-4-yne, in which both the double and triple bonds are encumbered, and one methylene doubly activated toward hydrogen abstraction, most of the products (**37–39**) are derived from abstraction.



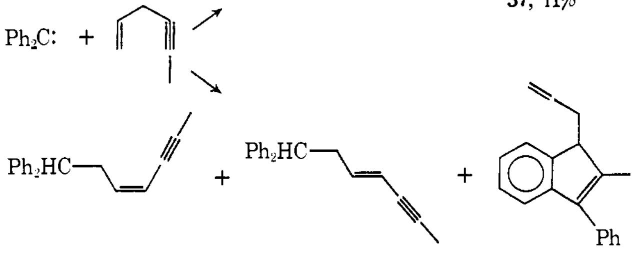
33, 42%

34, 43%

35, 15%

36, 6%

37, 11%



38, 48%

39, 35%

In summary, we would propose that a variety of steric interactions is the determining factor in the addition of DPC to olefins, acetylenes, and enynes. These control the ratio of addition to abstraction in substituted olefins and the ratio of cyclopropene to indene in acetylenes. All these factors come into play in the reactions with enynes, and although the effects are clearly subtle, the broad outlines of control over the products are visible.

Experimental Section

General. Nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates A-60A instrument, operated at 40°. Unless otherwise noted, Spectrograde CCl_4 was used as the solvent, with *ca.* 2% TMS as internal standard (see Table III). Microtube spectra were also taken in CCl_4, but *ca.* 10% TMS was used. Mass spectra were obtained with an AEI-MS-9 spectrometer, and in-

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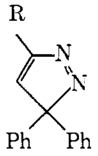
(43) L. P. Danilkina, I. A. D'yakonov, and G. I. Roslovtseva, *ibid.*, 1, 456 (1965).

(44) L. Vo-Quang and P. Cadiot, *C. R. Acad. Sci.*, 252, 3827 (1961).

(45) M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Amer. Chem. Soc.*, 94, 7469 (1972).

Table III. Nmr Spectra[a]

Compd	Spectrum
1	0.78 (3 H, br s), 0.88 (6 H, s), 1.24 (1 H, q), 6.9–7.2 (10 H, m)
2	0.98 (3 H, d), 1.52 (3 H, s), 2.7–3.4 (1 H, m), 3.6–3.9 (1 H, m), 4.5–4.9 (2 H, m), 6.8–7.4 (10 H, m)
3	1.05 (6 H, s), 3.72 (1 H, s), 4.8–5.2 (2 H, m), 5.8–6.2 (1 H, m), 7.0–7.4 (10 H, m)
4	1.55 (3 H, s), 1.62 (3 H, s), 2.5–2.9 (2 H, m), 2.90 (1 H, t), 4.9–5.2 (1 H, m), 7.15 (10 H, s)
5	1.18 (6 H, s), 1.68 (3 H, s), 4.08 (1 H, s), 4.7–4.8 (2 H, m), 7.0–7.3 (10 H, m)
6	1.38 (3 H, s), 1.53 (6 H, s), 3.74 (2 H, d), 4.02 (1 H, tr), 7.15 (10 H, s)
7	0.96 (6 H, s), 1.0–1.5 (4 H, m), 7.0–7.3 (10 H, m)
8	0.8–2.0 (8 H, m), 7.0–7.3 (10 H, m)
9	0.94 (3 H, d), 2.7–3.3 (1 H, m), 3.59 (1 H, d), 4.7–5.1 (2 H, m), 5.4–5.9 (1 H, m), 7.16 (10 H, m)
10	1.4–1.6 (3 H, m), 2.6–2.9 (2 H, m), 3.95 (1 H, tr), 5.28 (2 H, m), 7.18 (10 H, s)
11	1.4–1.6 (3 H, m), 2.6–2.9 (2 H, m), 3.95 (1 H, tr), 5.28 (2 H, m), 7.18 (10 H, s)
12	1.00 (6 H, s), 1.14 (2 H, s), 6.7–7.3 (10 H, m)
13	0.91 (3 H, d), 1.0–1.3 (2 H, m), 1.5–1.8 (1 H, m), 7.1–7.3 (10 H, m)
14	1.10 (2 H, s), 1.2–1.9 (10 H, m), 6.8–7.5 (10 H, m)
15	1.2–2.0 (8 H, m), 2.64 (2 H, d), 4.09 (1 H, tr), 6.9–7.3 (10 H, m)
16 (cis + trans)	1.62 (0.647 H, d), 1.84 (0.353 H, d), 2.78 (1 H, br d), 6.6–7.2 (15 H, m)
17a	1.22 (3 H, d), 3.47 (1 H, d of q), 6.3 (1 H, d), 7.0–7.7 (9 H, m)
17b	1.09 (9 H, s), 3.24 (1 H, d), 6.43 (1 H, d), 7.0–7.7 (9 H, m)
18a	2.15 (3 H, d), 5.94 (1 H, q), 7.45 (10 H, s)
18b	1.19 (9 H, s), 6.79 (1 H, s), 7.1–7.3 (10 H, m)
	R = *t*-Bu 1.28 (9 H, s), 6.61 (1 H, s), 7.0–7.5 (10 H, m)[b] R = CH_3 2.42 (3 H, d), 6.82 (1 H, q), 7.17 (10 H, s)
23	1.32 (3 H, d), 2.07 (3 H, d), 3.24 (1 H, q of q), 7.0–7.5 (9 H, m)
24	2.13 (6 H, s), 6.9–7.3 (10 H, m)
25	1.71 (3 H, tr), 2.75 (1 H, m), 4.50 (2 H, m), 7.0–7.3 (10 H, m)
28	1.47 (3 H, d), 1.73 (3 H, d), 2.8–3.2 (1 H, m), 4.59 (1 H, br s), 7.18 (10 H, s)
29	1.08 (3 H, d), 1.51 (3 H, d), 3.0–3.4 (1 H, m), 3.78 (1 H, d), 7.1–7.3 (10 H, m)
30	1.04 (3 H, tr), 1.46 (3 H, d), 1.8–2.1 (2 H, m), 3.0–3.4 (1 H, m), 4.58 (1 H, d), 7.14 (10 H, s)
31	0.88 (3 H, tr), 1.08 (3 H, d), 1.8–2.2 (2 H, m), 3.0–3.3 (1 H, m), 3.78 (1 H, d), 7.0–7.4 (10 H, m)
32	1.18 (3 H, s), 1.48 (2 H, q), 1.80 (1 H, s), 7.0–7.6 (10 H, m)
33	0.90–1.3 (5 H, m), 1.78 (1 H, tr), 2.16 (2 H, tr), 7.0–7.4 (10 H, m)
34	1.8–2.3 (4 H, m), 3.3–3.7 (1 H, m), 4.8–5.3 (3 H, m), 6.51 (1 H, d), 7.1–7.7 (10 H, m)
35	2.4–2.8 (2 H, m), 3.58 (1 H, m), 4.6–5.6 (5 H, m), 7.18 (10 H, s)
36	1.1–1.4 (3 H, m), 1.74 (3 H, tr), 1.8–2.0 (2 H, m), 7.0–7.4 (10 H, m)
37	1.78 (3 H, d), 3.0–3.3 (1 H, d), 4.6–6.3 (4 H, m), 7.21 (10 H, s)
38	1.79 (3 H, d), 2.97–3.09 (2 H, d of d), 4.02 (1 H, tr), 5.4–5.9 (2 H, m), 7.14 (10 H, s)
39	1.54 (3 H, d), 3.9–4.2 (3 H, m), 4.8–5.9 (3 H, m), 7.0–7.4 (9 H, m)

[a] Reported in δ as ppm from TMS as internal standard in CCl_4 solution: s = singlet, d = doublet, tr = triplet, q = quartet, m = multiplet, br = broad. [b] In C_6D_6.

Table IV. Infrared Spectra[a]

Compd	Spectrum
1	3050 (m), 3010 (m), 2980 (m), 2930 (s), 2920 (s), 2860 (m), 1595 (m), 1490 (s), 1445 (m), 1365 (m), 1030 (m), 790 (s), 765 (s), 750 (s), 710 (s)
12	3030 (s), 2995 (s), 2945 (s), 2910 (s), 2838 (s), 1580 (s), 1410 (s), 1425 (s), 1360 (m), 1355 (m), 1105 (m), 1065 (m), 1055 (m), 1010 (m), 985 (w), 940 (w), 905 (m)
28	2040 (s)
29	3080 (m), 3050 (s), 3000 (s), 2980 (s), 2920 (s), 2903 (s), 1950 (w), 1810 (w), 1595 (m), 1490 (s), 1450 (s), 1372 (m), 1210 (s), 1072 (m), 1025 (m), 925 (m), 845 (w), 700 (s)
30	3090 (s), 3079 (s), 3021 (s), 2981 (s), 2931 (s), 1964 (m), 1944 (w), 1878 (w), 1805 (w), 1716 (m), 1599 (s), 1495 (s), 1451 (s), 1366 (m), 1324 (m), 1215 (m), 1074 (s), 1027 (s), 1022 (m)
31	3085 (s), 3055 (s), 3025 (s), 2970 (s), 2930 (s), 2870 (s), 1597 (m), 1491 (s), 1449 (s), 1374 (m), 1376 (m), 1074 (m), 1029 (m)
32	3305 (s), 3075 (s), 3050 (s), 3015 (s), 2995 (s), 2975 (s), 2920 (s), 2895 (m), 2860 (m), 2103 (s), 1960 (w), 1945 (w), 1890 (w), 1875 (w), 1800 (w), 1721 (m), 1666 (m), 1598 (s), 1491 (s), 1449 (s), 1381 (m), 1276 (m), 1231 (m), 1215 (m), 1081 (s), 1041 (w), 1025 (m), 1020 (s), 946 (m), 920 (m), 690 (s)
33	3303 (s), 3089 (s), 3058 (s), 3020 (s), 2995 (m), 2920 (s), 2850 (m), 2115 (m), 1945 (w), 1800 (w), 1635 (w), 1595 (s), 1575 (m), 1545 (m), 1490 (s), 1450 (s), 1440 (s), 1425 (m), 1385 (w), 1315 (m), 1245 (m), 1055 (m), 1025 (m), 980 (m), 910 (m), 700 (s)
34	3060 (s), 3050 (s), 3005 (s), 2960 (m), 2905 (s), 2840 (s), 1945 (w), 1900 (w), 1880 (w), 1640 (s), 1595 (m), 1570 (m), 1545 (m), 1490 (s), 1460 (s), 1442 (s), 1412 (w), 1348 (m), 1300 (m), 1250 (w), 1070 (m), 1025 (m), 1018 (m), 985 (m), 905 (s), 865 (w), 700 (s)
35	3080 (s), 3055 (s), 3020 (s), 2975 (m), 2965 (m), 2905 (m), 1960 (m), 1735 (m), 1636 (m), 1595 (m), 1545 (m), 1490 (s), 1450 (s), 1260 (m), 1120 (m), 1075 (m), 1030 (m), 990 (m), 915 (m), 700 (s)
39	3080 (s), 3045 (s), 3010 (s), 2915 (s), 2845 (m), 1940 (w), 1800 (w), 1640 (m), 1599 (m), 1585 (m), 1495 (s), 1450 (s), 1400 (m), 1080 (m), 1033 (m), 980 (s), 920 (s), 700 (s)

[a] As CCl_4 solutions. Reported in cm^{-1}: s = strong, m = medium, w = weak.

frared spectra were taken on a Perkin-Elmer 237-B grating instrument (Table IV).

Analyses were performed by either Galbraith Laboratories, Knoxville, Tenn., or Atlantic Microlabs, Inc., Atlanta, Ga.

Gas chromatograph analyses (vpc) and collections were performed on a Varian Aerograph A-90-P instrument (thermal conductivity detector). Copper tubing (0.25 in.) was used for packing the columns, and helium was used as the carrier gas.

Yields. In most cases, yields of crude hydrocarbons isolated after chromatography on Al_2O_3 are reported. This is followed by a breakdown of the relative yields of these crude, volatile hydrocarbons. The chromatographically detected products account for all but traces of the crude volatile hydrocarbons.

Gas Chromatography Conditions:

A. 2-m 10% Dow Corning 710 silicone oil on 60–80 Chromosorb W, with a He flow of 100 ml/min.

B. 1-m 10% Dow Corning 710 silicone oil on 60–80 Chromosorb W, with a He flow of 100 ml/min.

C. 1-ft 10% FFAP on 60–80 Chromosorb P with a He flow of 100 ml/min.

D. 1-m 10% SE-30 silicone oil column on 60–80 Chromosorb P with a He flow of 115 ml/min.

E. 1-ft 20% FFAP on 60–80 Chromosorb P with a He flow of 100 ml/min.

Preparation of Diphenyldiazomethane (DPDM). This material was prepared by the yellow mercuric oxide oxidation of benzophenone hydrazone.[46]

Irradiation of DPDM in Propylene. A solution of 500 mg of DPDM in 10 ml of propylene was sealed under N_2 in a Pyrex tube

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(46) L. I. Smith and K. L.Howard, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 351.

and irradiated with two G.E. sun lamps for 12 hr. After evaporation of the solvent, the crude reaction mixture was examined by nmr spectroscopy. The adduct was isolated by chromatography on a 20 × 200 mm Al_2O_3–hexane column. Gas chromatographic analysis on column A at 198° (retention time 3.1 min)[47] revealed the adduct in 45% yield.

Irradiation of DPDM in Isobutylene. A solution of 258 mg of DPDM in 10 ml of isobutylene was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Gas chromatographic analysis and collection on column B at 172° (retention time 7 min) yielded the adduct in 57% yield.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.67; H, 8.34.

Irradiation of DPDM in *trans*-2-Butene.[6-9] A solution of 248 mg of DPDM in 10 ml of *trans*-2-butene was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Gas chromatographic analysis and collection on column A at 158° resulted in *trans*- and *cis*-2,3-dimethyl-1,1-diphenylcyclopropane (retention time 11.3 min, 22%), 1,1-diphenyl-2-methyl-3-butene (retention time 14.3 min, 27.6%), *trans*-1,1-diphenyl-3-butene (retention time 18.7 min, 44.2%), and *cis*-1,1-diphenyl-3-butene (retention time 20.3 min, 6.2%).

Irradiation of DPDM in 1-Butene. A solution of 258 mg of DPDM in 10 ml of 1-butene was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromatography on Al_2O_3–hexane gave 151 mg (51.1%) of crude hydrocarbons, and gas chromatographic analysis and collection on column A at 178° gave the following products: **8** (retention time 26 min, 74%), **9** (retention time 23 min, 11%), **11** (retention time 31 min, 8%), and **10** (retention time 34 min, 7%).

Anal. Calcd for $C_{17}H_{18}$ (**8**): C, 91.84; H, 8.16. Found: C, 91.78; H, 8.21.

Irradiation of DPDM in 3-Methyl-1-butene. A solution of 239 mg of DPDM in 10 ml of 3-methyl-1-butene was sealed under N_2 in a Pyrex tube and irradiated for 12 hr with two G.E. sun lamps. Chromatography on Al_2O_3–hexane gave 121 mg (41.6%) of crude hydrocarbons. Gas chromatographic analysis and collection on column A at 151° gave the following products: **7** (retention time 20 min, 52.5%), **3** (retention time 21.7 min, 14.9%), and **4** (retention time 29.4 min, 32.6%). Precise mass (**7**), 236.156063 (calcd for $C_{18}H_{20}$, 236.156493). Precise mass (**4**), 236.156282.

Irradiation of DPDM in 2-Methyl-2-butene. A solution of 210 mg of DPDM in 10 ml of 2-methyl-2-butene was sealed under N_2 in a Pyrex tube and irradiated for 12 hr with two G.E. sun lamps. Chromatography on Al_2O_3–hexane resulted in 108 mg (42.3%) of crude hydrocarbons. Gas chromatographic analysis and collection on column A at 175° led to the following products: **1** (retention time 14 min, 8.1%), **2** (retention time 15 min, 22.2%), **3** (retention time 16.5 min, 18.0%), and **4** (retention time 22 min, 51.7%). Precise mass (**1**), 236.156063.

Irradiation of DPDM in 2,3-Dimethyl-2-butene. A solution of 253 mg of DPDM in 10 ml of 2,3-dimethyl-2-butene was sealed under N_2 in a Pyrex tube and irradiated for 12 hr with two G.E. sun lamps. Chromatography on Al_2O_3–hexane resulted in 140 mg (43.1%) of crude hydrocarbons. Gas chromatographic analysis and collection on column A at 170° led to **5** (retention time 14.5 min, 34%) and **6** (retention time 16.2 min, 66%).

Anal. Calcd for $C_{19}H_{22}$ (**6**): C, 91.14; H, 8.86. Found: C, 90.98; H, 8.93. Precise mass (**5**), 250.172238 (calcd, 250.172142).

Irradiation of DPDM in Methylenecyclohexane. A solution of 239 mg of DPDM in 10 ml of methylenecyclohexane was sealed under N_2 in a Pyrex tube and irradiated for 12 hr with two G.E. sun lamps. Chromatography on Al_2O_3–hexane gave 159 mg (49.3%) of crude hydrocarbons. Gas chromatographic analysis and collection on column B at 200° led to **14** (retention time 23 min, 86.5%) and **15** (retention time 25 min, 13.5%). *Anal.* Calcd for $C_{20}H_{22}$ (**14**): C, 91.61; H, 8.39. Found: C, 91.23; H, 8.64.

Irradiation of DPDM in *cis*-β-Deuteriostyrene. A solution of 440 mg of DPDM in 1.8 g of *cis*-β-deuteriostyrene[23,24] was sealed under N_2 in a Pyrex tube and irradiated for 19 hr with two G.E. sun lamps. The excess styrene was removed at room temperature at the vacuum pump to give crude product which was analyzed by nmr spectroscopy (cis:trans = 63:37). Purification on Al_2O_3–hexane gave 440 mg (71.5%) of crude hydrocarbon (cis:trans = 64.7:35.3).

Irradiation of DPDM in *cis*-β-Deuteriostyrene and Hexafluorobenzene. Duplicate irradiations were run as above with varying amounts of hexafluorobenzene added. Recovered solvent was not isomerized.

Preparation of *cis*-4-Deuterio-3,3,5-triphenylpyrazoline. A solution of 500 mg of DPDM and 450 mg of *cis*-β-deuteriostyrene was allowed to stand in the dark for 4 days. After removal of the solvent at room temperature, spectral analysis of the crude product revealed the pyrazoline. Attempted purification on silica gel–5% ether–hexane led to *cis*-3-deuterio-1,1,2-triphenylcyclopropane, mp 51–52° (lit.[48] mp 51–52°), after recrystallization from methanol.

Irradiation of *cis*-4-Deuterio-3,3,5-triphenylpyrazoline. A solution of 100 mg of pyrazoline in 0.5 ml of benzene-d_6 was irradiated in an nmr tube with a G.E. sun lamp for 24 hr. No change occurred. Substitution of a 450-W medium-pressure mercury arc led to cyclopropanes in the ratio cis:trans = 55:45.

Irradiation of DPDM in Propyne. A solution of 800 mg of DPDM in 10 ml of propyne was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromatography on Al_2O_3–hexane gave 417 mg (52.5%) of crude 1-methyl-3-phenylindene (**17a**). Gas chromatographic analysis on column C at 158° (retention time 3 min) revealed only the known[49] indene.

Irradiation of *cis*- and *trans*-3-Deuterio-1,1,2-triphenylcyclopropane. A solution of 100 mg of cyclopropanes (cis:trans = 64.7:35.3) was dissolved in benzene and irradiated for 16 hr with a G.E. sun lamp. Nmr analysis showed cis:trans = 64:36.

Irradiation of DPDM in 3,3-Dimethyl-1-butyne. A solution of 300 mg of DPDM in 10 ml of 3,3-dimethyl-1-butyne was sealed under nitrogen and irradiated for 10 hr with two G.E. sun lamps. Gas chromatography on column C at 172° (125 ml/min) yielded 187 mg (49.0%) of **17b** (retention time 7 min).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.72; H, 81.32.

Irradiation of DPDM in Phenylacetylene. A solution of 500 mg of DPDM and 5 g of freshly distilled phenylacetylene in 5 ml of benzene was irradiated under nitrogen with two G.E. sun lamps for 12 hr. After removal of the solvents at the vacuum pump, nmr analysis of the crude material revealed 1,3-diphenylindene (**17c**)[49] as the only detectable product.

Preparation of 3,3-Diphenyl-5-methyl-3*H*-pyrazole. A solution of 500 mg of DPDM in 10 ml of propyne was sealed in a Pyrex tube and allowed to stand in the dark for 5 weeks. Removal of the solvent left a red-orange oily residue which was shown by spectral analysis to be crude pyrazole.

Irradiation of 3,3-Diphenyl-5-methyl-3*H*-pyrazole. A solution of 100 mg of pyrazole in 5 ml of hexadeuteriobenzene was irradiated with a medium-pressure mercury arc. The photolysis was monitored by nmr spectroscopy. At the end of 14.5 hr all the pyrazole was gone and 3,3-diphenyl-1-methylcyclopropene (**18a**) and 3-methyl-1-phenylindene (**17a**)[48] were formed in the ratio 2:1. Chromatography on silica gel–hexane gave pure cyclopropene.

Anal. Calcd for $C_{16}H_{14}$ (**18a**): C, 93.16; H, 6.84. Found: C, 92.96; H, 6.98.

Benzophenone-Sensitized Photolysis of 3,3-Diphenyl-5-methyl-3*H*-pyrazole. A solution of 100 mg of pyrazole and 30 mg of benzophenone in 5 ml of hexadeuteriobenzene was irradiated under nitrogen for 7 hr in a Pyrex tube with a medium-pressure mercury arc. At the end of the irradiation period the ratio of cyclopropene to indene was 1.3:1.

3,3-Diphenyl-5-*tert*-butyl-3*H*-pyrazole. A solution of 1 g of DPDM in 5 ml of *tert*-butylacetylene was allowed to stand at room temperature in the dark for 6 days. The resulting crystalline mass was washed with ice cold pentane until the purple color of DPDM was gone. Recrystallization from cyclohexane gave analytically pure material, mp 141–143°.

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29. Found: C, 82.34; H, 7.37.

Irradiation of 3,3-Diphenyl-5-*tert*-butyl-3*H*-pyrazole. A solution of 32 mg of pyrazole in 200 ml of hexadeuteriobenzene was irradiated with a medium-pressure mercury arc for 1 hr. Nmr spectroscopy showed no pyrazole and a 1.4:1 mixture of indene (**17b**) and cyclopropene (**18b**). Addition of benzophenone and further photolysis did not change this ratio.

Anal. Calcd for $C_{19}H_{20}$ (**17b**): C, 91.73; H, 8.12. Found: C, 91.69; H, 8.13. Found (**17b** + **18b**): C, 91.88; H, 8.15.

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[47] H. M. Waborsky and A. E. Young, *J. Amer. Chem. Soc.*, 86, 3288 (1964).

[48] B. S. Gorton, *J. Org. Chem.*, 30, 648 (1965).

[49] B. Cheminat and R. Rambaud, *C. R. Acad. Sci., Ser. C*, 268, 724 (1969).

Irradiation of 3,3-Diphenyl-1-methylcyclopropene. A hexadeuteriobenzene solution of 30 mg of cyclopropene was irradiated through Pyrex with a medium-pressure mercury arc for 12 hr. At the end of this time no indene had formed.

Benzophenone-Sensitized Irradiation of 3,3-Diphenyl-1-methylcyclopropene. To the above solution of cyclopropene in hexadeuteriobenzene was added 20 mg of benzophenone. The solution was irradiated with the medium-pressure mercury arc for 12 hr. Again no indene was formed.

DPDM-Sensitized Irradiation of 3,3-Diphenyl-1-methylcyclopropene. A solution of 30 mg of cyclopropene and 15 mg of DPDM in 5 ml of hexadeuteriobenzene was irradiated under nitrogen by two G.E. sun lamps until the purple color of DPDM had disappeared (2 hr). The cyclopropene was not converted to indene.

Pentadeuteriobromobenzene. To 20 g of hexadeuteriobenzene and 1 g of iron filings stirred at 70° was added dropwise 38 g of bromine. HBr evolution was rapid. The reaction mixture was stirred at 80° until evolution of HBr ceased, and dumped into water. The organic layers were extracted with 2 × 50 ml of ether and 1 × 50 ml of saturated NaCl. After drying, distillation yielded 20.9 g of pentadeuteriobromobenzene (bp 153–155°).

Pentadeuteriobenzoic Acid. A Grignard reagent was prepared from 20 g of the above bromobenzene. The brown solution was poured over Dry Ice and allowed to warm to room temperature during which time the ether evaporated. The solid sludge was treated with 1 *M* NaOH, filtered, and washed with 2 × 100 ml of ether. The clear solution was acidified with 3 *M* HCl and the precipitated benzoic acid (9.7 g, mp 120–121°) recrystallized from water and dried.

Pentadeuteriobenzophenone. To 9.7 g of the above benzoic acid in 150 ml of anhydrous ether under nitrogen in a three-necked flask fitted with overhead stirrer, reflux condenser, and addition funnel was added dropwise 80 ml of a 2.14 *M* solution of phenyllithium (Alfa Inorganics). A dense white precipitate formed immediately, much of which redissolved as more phenyllithium was added. Following the addition, the solution was allowed to stir at room temperature for 4 hr. The slurry was poured into 1 l. of ice-cold 3 *M* HCl. The organic layer was washed with 3 × 150 ml of water, dried, and concentrated. The crude material was used to prepare the hydrazone and diazo compound.[46]

Irradiation of DPDM-d_5 in Propyne or 3,3-Dimethylbutyne. A solution of 400 mg of DPDM-d_5 in 10 ml of propyne was sealed in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. The solvent was allowed to evaporate and the crude residue analyzed by nmr spectroscopy. An average of two runs was used for the determination of the isotope effects. An attempt to purify the crude reaction mixture by chromatography on Al_2O_3 resulted in a statistical scrambling of the deuterium between the 1 and 3 positions. Chromatography on Florisil did not rearrange deuterium. Irradiations in 3,3-dimethylbutyne were run in a similar manner.

Irradiation of DPDM in 2-Butyne. A solution of 500 mg of DPDM in 12 ml of 2-butyne was sealed under nitrogen in a Pyrex tube and irradiated with two G.E. sun lamps for 18 hr. After nmr analysis of the crude product, gas chromatography on column D at 126° gave a mixture of: 2,3-dimethyl-1-phenylindene (**23**) (retention time 35 min, 1.6%), 1,1-diphenyl-2,3-dimethylcyclopropene (**24**) (retention time 31 min, 73%), and **25** (retention time 31 min, 25.4%).

Anal. Calcd for $C_{17}H_{16}$ (**24** + **25**): C, 92.68; H, 7.32. Found: C, 92.49; H, 7.41. Found (**23**): C, 92.65; H, 7.40.

Irradiation of DPDM in 2-Pentyne. A solution of 500 mg of DPDM in 3 g of 2-pentyne was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromatography on Al_2O_3–hexane yielded 250 mg (45.1%) of crude hydrocarbons. Gas chromatographic analysis and collection on column E at 185° gave **28** (retention time 9.4 min, 24.8%) and **29** (retention time 11.3 min, 75.4%). Precise mass (**29**), 234.140519 (calcd $C_{18}H_{18}$, 234.140844).

Preparation of Diphenyl-2-pentylcarbinol. A 250-ml, three-necked, round-bottom flask equipped with addition funnel, condenser, and magnetic stirring bar was flushed with N_2 for 15 min. Mg turnings (3.2 g, 0.133 mol) were placed in the flask and covered with about 10 ml of anhydrous ether. Added dropwise was a solution of 20 g (0.133 ml) of 2-bromopentane and 25 ml of ether. Once the reaction started, 15 ml of additional ether was added to the pot. The addition of 2-bromopentane solution took about 1 hr. After 0.5 hr additional stirring a solution of 24 g (0.13 mol) of benzophenone in 50 ml of ether was added. The light brown solution was gently refluxed for 2 hr, cooled to 0°, and carefully hydrolyzed with 100 ml of 10% H_2SO_4. The two layers were separated and the ether was washed two times with 10% H_2SO_4 and saturated NaCl and dried over Na_2SO_4. Removal of the ether left a light yellow, low melting reaction mixture which was used in the next step.

Preparation of 1,1-Diphenyl-2-methyl-1-pentene. The crude carbinol from the previous reaction was vaccum distilled from a small spatula full of ground anhydrous $NaHSO_4$. The only fraction collected was a colorless liquid, 9.0 g, bp 130–139° (0.25 Torr). This fraction was placed on a 35 × 350 mm alumina column and eluted with hexane to remove benzophenone which had codistilled with the olefin. The chromatography gave 4.5 g of a colorless liquid which was identified as 1,1-diphenyl-2-methyl-1-pentene.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.40; H, 8.57.

1,1-Diphenyl-2-methylpentane. A solution of 1 g of 1,1-diphenyl-2-methyl-1-pentene in 50 ml of ethanol was placed in a pressure bottle with 100 mg of PtO_2. Hydrogenation in a Parr hydrogenator was stopped after 4.5 hr when the uptake of hydrogen ceased. Gas chromatography on column D at 180° gave 1,1-diphenyl-2-methylpentane (retention time 5.7 min).

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H. 9.30. Found: C, 90.63; H, 9.31.

Hydrogenation of 2-Benzhydryl-2,3-pentadiene and 2-Benzhydryl-3-pentyne. A mixture of 37 mg of the two hydrocarbons was hydrogenated over PtO_2 in ethanol to give 2-benzhydrylpentane identical with that previously made.

Irradiation of DPDM in 3-Hexyne. A solution of 300 mg of DPDM in 3 ml of 3-hexyne was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromatography on Al_2O_3–hexane gave 200 mg (57.5%) of crude hydrocarbons. Gas chromatographic analysis and collection on column E at 180° gave: **30** (retention time 3.5 min, 31%), **31** (retention time 6 min, 64%), and an unidentified product (retention time 8 min, 15%). Precise mass (**30**) 248.156167 (calcd for $C_{19}H_{20}$, 248.156493). Precise mass (**31**), 248.156997.

Irradiation of DPDM in Phenylacetylene and *cis*-β-Deuteriostyrene. A solution of 130 mg of DPDM in 350 mg of *cis*-β-deuteriostyrene and 720 mg of phenylacetylene was sealed in a Pyrex tube and irradiated for 12 hr with a G.E. sun lamp. Analysis of the crude product by nmr revealed the relative rate of addition to styrene to be three times that to acetylene.

Irradiation of DPDM in Propyne and *cis*-β-Deuteriostyrene. A solution of 140 mg of DPDM in 580 mg of *cis*-β-deuteriostyrene and an equal volume of propyne was sealed under nitrogen in a Pyrex tube and irradiated for 20 hr with a G.E. sun lamp. Analysis of the crude product revealed *cis*- and *trans*-**16** and only traces of **17a**.

Irradiation of DPDM in Propene and Propyne. A solution of 300 mg of DPDM in 10 ml of a calibrated, approximately 37:63 mixture of propene and propyne was sealed under nitrogen and irradiated with two G.E. sun lamps for 12 hr. Analysis by nmr and correction for the relative amounts of substrate gave relative rates of addition (82:18).

Irradiation of DPDM in 2-Methyl-1-buten-3-yne. A solution of 575 mg of DPDM in 10 ml of 2-methyl-1-buten-3-yne was sealed under N_2 in a Pyrex tube and irradiated for 12 hr with two G.E. sun lamps. Chromatography on Al_2O_3–hexane gave 310 mg (54.6% of crude hydrocarbons). Gas chromatography on column E at 185° gave 1,1-diphenyl-2-ethynyl-2-methylcyclopropane (**32**).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.81; H, 6.93.

Irradiation of DPDM in 1-Hexen-4-yne. A solution of 500 mg of DPDM in 4 g of 1-hexen-4-yne was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromtaography on Al_2O_3–hexane gave 309 mg (48.0%) of crude hydrocarbons. Gas chromatography on column E at 185° gave: **37** (retention time 3.5 min, 11%), **39** (retention time 5 min, 35%), **36** (retention time 8 min, 6%), *cis*-**38** (retention time 10 min, 17%), and *trans*-**38** (retention time 17 min, 31%). Precise mass (**37**), 246.14151 (calcd for $C_{19}H_{18}$, 246.14084); (**36**), 246.14013; (*cis*-**38**) 246.140369; (*trans*-**38**), 246.141051.

Anal. Calcd for $C_{19}H_{18}$ (**39**): C, 91.47; H, 8.53. Found: C, 92.45; H, 7.33.

Irradiation of DPDM in 1-Hexen-5-yne. A solution of 500 mg of DPDM in 2 g of 1-hexen-5-yne was sealed under N_2 in a Pyrex tube and irradiated with two G.E. sun lamps for 12 hr. Chromatography on Al_2O_3–hexane gave 200 mg (31.5%) of crude hydrocarbons. Gas chromatography on column E at 180° gave: **35** (retention time 7 min, 15%), **33** (retention time 9 min, 42%), and **34** (retention time 13.5 min, 43%). Precise mass (**35**), 246.140369 (calcd for $C_{19}H_{18}$, 246.14084); (**33**), 246.14105; (**34**), 246.13989.

Photochemical Stability of the Cyclopropanes. In a typical experiment, **8** (along with small amounts of isomers 9, **10**, and **11**) was dissolved in benzene-d_6 and irradiated with two G.E. sun lamps for 12 hr. Nmr analysis revealed no change in the isomer distribution or absolute amount of **8**. Addition of benzophenone or DPDM was without effect as was duration of irradiation.

Methyleneketenes by Irradiation of α,β-Unsaturated Ketones

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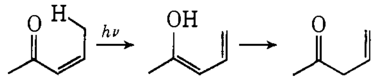
Abstract: Irradiation of 3-methylenedibenzobicyclo[2.2.2]octadien-2-one (**17**, $R_1 = R_2 = H$) in methanol gave mainly (>93%) 2-carbomethoxydibenzobicyclo[2.2.2]octa-5,7-diene (**18**); in ether containing diethylamine the product was the corresponding amide. A mechanism involving α′ cleavage, electron delocalization to the α,β-double bond, and rebonding between the α′- and β-carbon atoms to form ketene **19** is supported by experiments with methyl labeling at the bridgehead positions. Thus **21** gave ester **22** and **23** gave ester **24**. A small amount (0.6%) of dianthracene was isolated from the irradiation of **17**, suggesting that some small amount of α,β′-bond cleavage to methyleneketene occurred. This latter path became considerably more important on β-phenyl substitution. Irradiation of 3-benzylidenedibenzobicyclo[2.2.2]octadien-2-one (**17**, $R_1 = H$, $R_2 = C_6H_5$) in methanol gave dianthracene and methyl *cis*- and *trans*-cinnamates in 42% yield; the cinnamates presumably arise from trapping of benzylideneketene by methanol. In addition, a 58% yield of *cis*- and *trans*-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octa-5,7-dienes (**25c** and **25t**) was obtained through intramolecular rearrangement. Thus, α,β-unsaturated ketones of the type **17** undergo α′ cleavage in preference to other possible reaction paths. This may be followed by rearrangement to a bicyclic ketene (**19**) or fragmentation to a methyleneketene (**26**) and anthracene. These paths compete with the more common cis–trans isomerism of acyclic enones, probably because of stabilization of the α′ radical by aryl rings.

A diverse number of inter- and intramolecular photochemical transformations are undergone by α,β-unsaturated ketones. Although the excitation energy always involves the same chromophore, the particular reaction path may depend upon the overall molecular structure, the solvent, the presence of another reactant, and the multiplicity of the excited state. Six distinct reaction types have been identified: (a) hydrogen abstraction, (b) dimerization, (c) oxetane formation, (d) photoisomerization, (e) cis–trans isomerization, and (f) α cleavage.[1]

Hydrogen abstraction may occur intramolecularly by the oxygen from a γ position to give a nonconjugated enone[2] (1 → 2) or from a γ′ position to give a cyclobutyl ketone (3 → 4).[3] Hydrogen abstractions from the β position (5 → 6)[4] or by the β-carbon atom (7 → 8)[5] are also known. Intermolecular hydrogen abstraction may be observed, particularly when the molecular geometry is detrimental to the intramolecular reaction; the net result is either reduction of the carbon–carbon double bond or addition of hydrogen and a radical to the double bond.[6]



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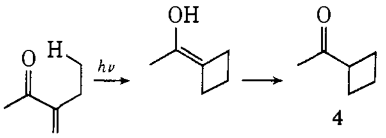

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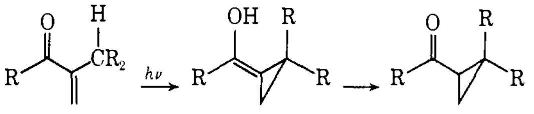

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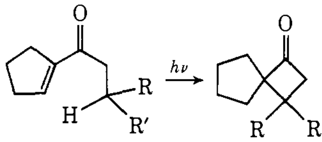

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When the carbon–carbon double bond of an enone is part of a five- or six-membered ring, and no γ hydrogens are available, the most frequently observed photochemical reaction is the formation of a cyclobutane dimer.[7] This cycloaddition may also occur with added olefins[8] or with a suitably located intramolecular double bond.[9] Cycloaddition may also occur at the carbon–oxygen double bond, resulting in an oxetane. The re-

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