and filtered to give 50 mg of light yellow product. A second recrystallization from ether gave a sample melting at 208–209°.

Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.24; H, 4.74. Found: C, 81.03; H, 4.93.

The uv spectrum of compound **14** in ether has maxima at 2070 Å (ϵ 4.3 × 10^4), 2250 (5 × 10^4), and 3085 (3 × 10^4). The 3085-Å band is very broad and tails into the visible. *cis*-Stilbene, except for additional fine structure, displays much the same spectrum: 2030 Å (ϵ 2.4 × 10^4), 2280 (1.6 × 10^4), and a broad absorption with maxima at 2941 (2.79 × 10^4) and 3080 (2.64 × 10^4).[27]

The *exo* configuration of the fused cyclobutene ring was assigned by comparing the pmr spectrum of **14** with that of 7,8-diphenyltricyclo[4.2.$1^{2,5}$.0]nona-3,7-diene.[28]

Deuterated Cyclopentadiene.—Sodium hydride (3 g) dispersed in mineral oil was carefully added with stirring to 20 ml of dry cyclopentadiene in 100 ml of ether. When hydrogen evolution ceased, 40 ml of deuterium oxide was added and the mixture was stirred vigorously for 2 hr. The ether–cyclopentadiene layer was then distilled under vacuum, dried over magnesium sulfate, and recycled. After three such treatments the ether layer contained about 2–3 ml of cyclopentadiene (based on glpc-peak areas).

Isolation of a small sample by preparative glpc and quantitative comparison of the C–D stretching *vs.* the C–H stretching in its ir spectrum led to the assignment of approximately 60% deuteration.

Registry No.—**1,** 15914-94-0; **3,** 17397-31-8; **4,** 17397-35-2; **5,** 17414-28-7; **7,** 17397-36-3; **8,** 17397-32-9; **9,** 17411-01-7; **10,** 17414-29-8; **11,** 17397-33-0; **12,** 17458-12-7; **13,** 17447-99-3; **14,** 17397-34-1.

(27) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 276, 277.

(28) G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

Cyclopentadienylidene. Stereochemistry of the Addition Reaction

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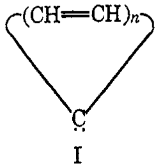
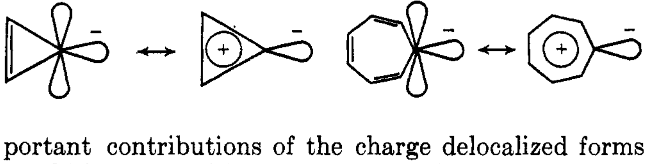
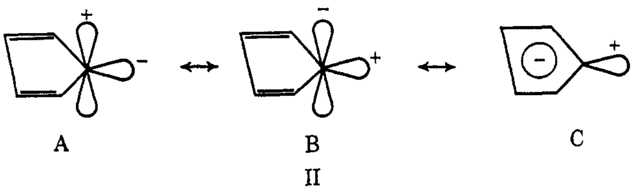
Photolysis of diazocyclopentadiene in *cis*- and *trans*-4-methylpentene-2 led to the formation of *cis*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6 and *trans*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6, respectively. No *cis* product was formed from the *trans* olefin, but some *trans* product was found in the product mixture from the *cis* olefin reaction. Under conditions where the spiro[2.4]heptadienes do not photointerconvert, the extent of formation of *trans* product from *cis* olefin is small (1–2%). This nonstereospecificity could not be greatly increased by carrying out the photolysis in large excesses of hexafluorobenzene or octafluorocyclobutane diluents, nor could it be much decreased by means of 2,5-dimethylhexadiene-2,4 or acrylonitrile diluents. It is concluded that the photolysis of diazocyclopentadiene leads to a singlet cyclopentadienylidene which reacts more rapidly with olefinic substrate than it crosses to its triplet ground state.

It is well known that a carbene's ability to discriminate between various olefinic substrates may be greatly enhanced by the proper choice of carbenic substituent groups, *e.g.*, chlorine or fluorine.[1] More recently, attempts have been made to generate carbenes in which unique chemistry might be anticipated due to the incorporation of the carbenic center in a potentially aromatic system. Three such systems, of basic structure I, have been studied. For I, $n = 1$, cyclopropenylidene, and I, $n = 3$, cycloheptatrienylidene, it was hoped that the singlet carbene would derive important stabilization from the aromaticity expressed by the resonance hybrids which are shown below. Important contributions of the charge delocalized forms would be signaled by *nucleophilic* behavior of the carbenes toward olefins. Thus far, in keeping with prediction, only olefins with electron-poor π bonds have proven to be suitable substrates for these systems.[2] For the system I, $n = 2$, cyclopentadienylidene, the situation is more complex. The ground state of the carbene is known to be a triplet in which one unpaired electron is localized in the in-plane sp^2 orbital, while the other electron is in the π system.[3] The singlet state of the carbene may be expressed as the resonance hybrid II. Although, ordinarily, a singlet carbene would be expected to adopt an electronic configuration in which the lone pair populates the inplane sp^2 orbital, IIA, rather than a p orbital, IIB, recent calculations indicate that the alternative configurations are within 0.2 eV. The resulting extensive configuration interaction will lead to mixing of IIA and IIB, and the singlet cyclopentadienylidene is therefore best represented as the entire resonance hybrid II.[4] An important question is: how much of a contribution is made by the charge delocalized canonical form IIC? Were II adequately



I





II

(1) R. A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967), and references therein.

(2) Cyclopropenylidene: see W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *J. Amer. Chem. Soc.*, **90**, 1849 (1968), and references therein. Cycloheptatrienylidene: see W. M. Jones and C. L. Ennis, *ibid.*, **89**, 3069 (1967); T. Mukai, T. Nazakawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968).

(3) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Amer. Chem. Soc.*, **86**, 2304 (1964).

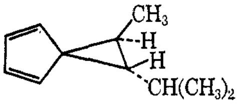
(4) Private communication from Professor Roald Hoffmann, Cornell University.

described by IIC alone, might it exhibit unique chemical reactivity? The olefin addition and C–H-insertion reactions of II have been studied, and its minimal discriminatory ability suggests it to be a poorly stabilized and highly reactive carbene.[5] No conclusions could be drawn about the extent of IIC's contribution to II from the reactivity data.[5] The data did suggest, however, that whereas the ground state of cyclopentadienylidene was a triplet, the species produced by photolysis of diazocyclopentadiene (DCPD) in olefinic solution at 25° was largely a singlet. Thus II added at identical rates to hexene-1 and styrene,[5] whereas a triplet carbene would be expected to discriminate in favor of styrene. On the other hand, generation of the carbene in *cis*-butene did lead to about 5–8% nonstereospecific addition.[6] Nonstereospecificity of a carbene–olefin addition reaction is generally associated with the intervention of a triplet carbene.

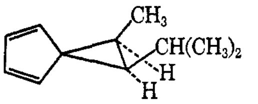
In order to learn more about the possible intervention of triplet cyclopentadienylidene, we made a close study of the stereochemistry of addition of cyclopentadienylidene to 4-methyl-*cis*-pentene-2.

Results

Photolysis of DCPD in *trans*- and *cis*-4-methylpentene-2 led to spiro[2.4]heptadienes III and IV, respectively. Both III and IV gave satisfactory elemental analyses. Their ir spectra were consonant with assigned structure, and in their uv spectra each exhibited the expected maximum and shoulder in the 230 and 260 mμ regions.[5] Both hydrocarbons showed significant uv absorption at 300 mμ (ϵ *ca.* 40) in pentane solution.



III



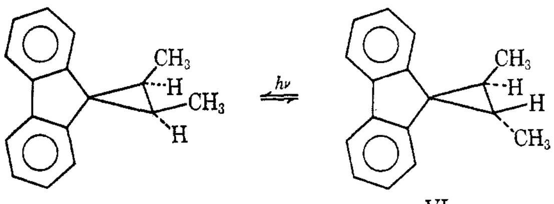
IV

The nmr spectrum of III (CCl$_4$) showed the vinyl protons as two multiplets centered at δ 6.34 and 6.06. The cyclopropyl protons and the isopropyl carbinyl proton appeared as a complex multiplet in the region 2.1–1.2. The lone methyl group was a doublet at 1.3, J = 6 cps. The isopropyl methyl groups were nonequivalent and appeared as two crude doublets at 1.05 and 0.80, J = 6 cps. The rather low-field absorption of the cyclopropyl protons relative to the alkyl protons has been noted previously in spiro[2.4]heptadienes.[5] Various area ratios for these signals were consonant with structure.

The nmr spectrum of IV (CCl$_4$) was similar. The vinyl protons appeared as three multiplets, centered at *ca.* δ 6.44, 6.16, and 5.88. (The areas of these multiplets were in the ratio 1:2:1.) The cyclopropyl and isopropyl carbinyl protons appeared as a complex multiplet in the region 2.38–1.50. The lone methyl group was a doublet centered at 1.33, J = 6 cps. The nonequivalent isopropyl methyls were crude doublets, centered at 1.05 and 0.84, J = 6 cps. It is interesting to note the large nonequivalence of the isopropyl methyl groups in III and IV. While not so large as that observed recently by Kajtár,[7] the magnitude of the nonequivalence deserves comment. Models suggest that steric hindrance to rotation of the isopropyl group about the ring-isopropyl–carbon bond is provided by interaction of the isopropyl methyls and the nearest neighbor vinyl proton. The isopropyl group is thus largely restricted to a conformation in which the magnetic nonequivalence of its methyl groups is amplified by the differential anisotropy of the cyclopentadiene π electrons.

With the characterization of III and IV completed, it was possible to show by glpc that, whereas no *cis* product, IV, was formed when DCPD was photolyzed in 4-methyl-*trans*-pentene-2, about 5% of *trans* product, III, was formed when DCPD was photolyzed in 4-methyl-*cis*-pentene-2. In this experiment, III was identified by comparison of its glpc retention time and ir spectrum with those of an authentic sample. This reaction, then, was nonstereospecific, and we subjected it to closer scrutiny.

Nonstereospecific Additions of II.—Mindful of the fact that the isomerization V ⇌ VI had been reported,[8] we examined the photostability of III and IV. In hexane solution, both III and IV, when subjected to unfiltered 2537 Å radiation, undergo photoreaction. There is a gradual appearance of the isomeric spiro[2.4]heptadiene, coupled with a loss of both isomers to unidentified products. After 41 hr of photolysis, only 12.8% of starting IV could be accounted for in terms of III and IV, and the isomer composition [III/(III + IV)] was 0.56. Under similar conditions, starting with pure III, after 50.5 hr of photolysis, 57% of the starting material could be accounted for in terms of III and IV, and the isomer composition was 0.43. Relative to the V–VI photointerconversion,[8] the present example is interesting since the light is here being absorbed directly by the diene system, rather than by the aromatic centers of a fluorene unit. A somewhat related photoisomerization has been reported by Pirkle.[9]



V VI

The observed photointerconversion of III and IV suggested that care would be necessary to ascertain the real extent of nonstereospecificity of the addition reactions of II. Indeed, photolysis of dilute cyclohexane solutions of IV (Pyrex test tube, 1 hr) with a G. E. sunlamp did afford up to 2% isomerization to III. The isomerization was reduced by use of a Corning, C.S. 3-94, uranium glass filter. Furthermore, in the presence of DCPD and the tarry by-products of its photodecomposition, the isomerization was completely suppressed, even when the irradiation time was extended to 2.5 hr.

The nonstereospecificity of addition of II to 4-methyl-*cis*-pentene-2 was determined from runs in which 50

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(5) R. A. Moss, *J. Org. Chem.*, **31**, 3296 (1966).

(6) See footnote 18 of ref 5. Professor Jones' observation has been confirmed in our laboratory.

(7) M. Kajtár and L. Radics, *Chem. Commun.*, 784 (1967).

(8) W. von E. Doering and M. Jones, Jr., *Tetrahedron Lett.*, 791 (1963).

(9) W. H. Pirkle and G. F. Koser, *ibid.*, 129 (1968).

mg of DCPD in 10 ml of olefin was photolyzed (Pyrex test tube) at 0° for 2.5 hr by a G. E. sunlamp (uranium glass filter). The product ratio III/(III + IV) was determined by glpc on a 100 ft SF-96 Golay column. The flame ionization detector was calibrated with prepared mixtures of III and IV, which were both stable to the analytical conditions. It was observed, however, that solutions of DCPD in 4-methyl-*cis*-pentene-2 when injected *directly* into the gas chromatograph gave product mixtures containing both III and IV in the distribution 28:72. This "nonstereospecific" reaction may reflect a vapor phase addition of II to the olefin leading to a "hot" IV, which can then isomerize to III.[10] Whatever the explanation for this phenomenon, it was essential that all DCPD was destroyed before product analyses were carried out. Product mixtures were checked for the absence of DCPD by ir.

Over six photolyses, III/(III + IV) ranged from 0.012 to 0.019. The average value was 0.016 ± 0.002. The extent of nonstereospecificity is thus quite small. The highest nonstereospecificity observed for the addition reaction was in the thermolysis of DCPD in 4-methyl-*cis*-pentene-2, in a sealed tube at 180° for 5 hr. The ratio, III/(III + IV), was 0.044 ± 0.003. The spiro[2.4]heptadienes were shown not to isomerize under these conditions; and the purity of the *cis*-olefin substrate was shown to be greater than 99% before and after the thermolysis. The even greater "nonstereospecificity" observed in the preparative-scale photolysis of DCPD (see above) can probably be ascribed to photoisomerization.

Nonstereospecificity under Other Conditions.— Some experiments aimed at increasing the nonstereospecific component of the addition reaction were carried out. Since triplet cyclopentadienylidene results when DCPD is photolyzed in a fluorocarbon matrix at 77°K,[3] we hoped that a similar reaction in a 4-methyl-*cis*-pentene-2 matrix would generate II which would cross to the triplet state without reacting. Cycles of photolysis, thawing, and recooling might then permit observation of nonstereospecific reaction of the triplet carbene. In this event, only a modest increase in nonstereospecificity was observed; the ratio III/(III + IV) was 0.025.

Photolyses of DCPD in mixtures of hexafluorobenzene and 4-methyl-*cis*-pentene-2 were also studied. It was hoped that the additive would function as an inert diluent, allowing singlet II to undergo enough fruitless collisions, such that an appreciable proportion would cross to the triplet ground state, leading to an enhancement of nonstereospecific addition. The data of Table I show that even under conditions where the hexafluorobenzene was present at 96 mol %, nonstereospecific addition remained minimal.

TABLE I

PHOTOLYSIS AT 0° OF DCPD IN MIXTURES OF HEXAFLUOROBENZENE AND 4-METHYL-*cis*-PENTENE-2[a]

Run	Mole fraction of hexafluorobenzene	III/(III + IV) × 100[b]
43	0.00	1.21
47	0.00	1.47
61	0.00	1.53
51	0.53	1.34
57	0.52	1.75
52	0.89	2.59
58	0.90	2.45
53	0.94	3.00
59	0.96	2.97

[a] DCPD concentration was 0.05–0.06 *M*. [b] Each value is considered accurate to ±5%.

A complication in these experiments arises in that hexafluorobenzene was observed *not* to be inert to II. Thus, at high mole fractions of diluent, a new product was observed in the chromatogram.[11]

In contrast, octafluorocyclobutane proved to be inert toward II, and a series of dilution experiments with this material were carried out in sealed pressure tubes at 0°. For unknown reasons, nonstereospecificity was somewhat greater in the pressure-tube runs than in the test-tube runs, but the data in Table II reveal that the dilution effect was again minimal.

TABLE II

PHOTOLYSIS AT 0° OF DCPD IN MIXTURES OF OCTAFLUOROCYCLOBUTANE AND 4-METHYL-*cis*-PENTENE-2[a]

Run	Mole fraction of octafluorocyclobutane	III/(III + IV) × 100[b]
95	0.00	2.51
97	0.00	2.42
85	0.52	2.56
98	0.88	2.66
99	0.95	2.95
101	0.98	3.13

[a] DCPD concentration was 0.02–0.03 *M*. [b] Each value is considered accurate to ±3%.

Acting on the possibility that the small nonstereospecificity which we did observe was due to triplet cyclopentadienylidene, we attempted to scavenge this species. These attempts failed. Thus, in mixtures of 4-methyl-*cis*-pentene-2 and 2,5-dimethylhexadiene-2,4 photolysis of DCPD led to unaltered product ratios. At diene mole fractions of 0.42 and 0.62, the ratio III/(III + IV) was 0.020 and 0.022, respectively. Similar experiments were carried out with an acrylonitrile diluent. The results were minimally successful, as shown in Table III.

TABLE III

PHOTOLYSIS AT 0° OF DCPD IN MIXTURES OF ACRYLONITRILE AND 4-METHYL-*cis*-PENENE-2[a]

Run	Mole fraction of acrylonitrile	III/(III + IV) × 100[b]
108	0.00	1.90
109	0.00	1.90
117	0.52	1.58
115	0.75	1.40
116	0.90	1.24
118	0.90	1.26

[a] DCPD concentration was *ca.* 0.05–0.06 *M*. [b] Each value is considered accurate to ±4%.

Finally, we might note that control experiments revealed no significant change in nonstereospecificity when the DCPD photolysis was carried out at five times the normal DCPD concentration, or when *p*-toluenesulfonyl azide (used in the preparation of

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[10] The liquid phase thermolysis of DCPD was also studied, see below.

[11] The reaction of II and hexafluorobenzene is described in detail by M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968). We thank Professor Jones for a preprint of this article.

DCPD, and a possible impurity) was deliberately added. No substantial stereochemical changes were observed when the photolysis was done under nitrogen, rather than air. The pentene substrates in the photolytic experiments could be recovered without evidence of isomerization after the photolyses.[12]

Discussion

The previous reactivity data[5] and the present stereochemical results are consistent with the idea that photolysis of DCPD in hydrocarbon solvents at ambient temperatures leads to a *singlet* cyclopentadienylidene, II, which inserts readily, and with little discrimination into saturated C–H bonds, and adds, with little selectivity and *high stereospecificity*, to carbon–carbon double bonds.

The major alternative, which must be seriously considered because of cyclopentadienylidene's known triplet ground state,[3] is that a substantial portion of its addition reaction proceeds *via* the triplet state. This seemed unlikely because addition to styrene proceeded at the same rate as addition to hexene-1,[5] and it is now seen to be still more unlikely in view of the high stereospecificity observed in the addition of II to 4-methyl-*cis*-pentene-2. The previously observed 8% nonstereospecificity in addition to *cis*-butene[6] is probably a consequence of product photoisomerization.

Some question can be raised as to whether the 98% stereospecificity here observed really rules out substantial triplet participation in the addition reaction. That gross nonstereospecificity during carbene–olefin addition reactions signals triplet intermediacy[13] seems to be generally accepted.[14] That the absence of substantial nonstereospecificity rules out significant incursion of a triplet carbene is a more tenuous hypothesis. To our knowledge, there is no known case in which a *triplet* carbene reacts with an olefin, *mainly* by addition to the double bond, without *gross* nonstereospecificity. Thus addition of fluorenylidene to 4-methyl-*cis*-pentene-2 occurred with formation of 45% *trans* product, which was increased to 75% in the presence of 90 mol % of hexafluorobenzene.[15] Biscarbomethoxycarbene added to 4-methyl-*cis*-pentene-2 with only 8% nonstereospecific product formation, but this was because the addition occurred primarily from the singlet state of the carbene; the triplet state, produced in a photosensitization experiment, added to the same olefin with the formation of 88% *trans*-cyclopropane.[16] Similar conclusions as to the nonstereospecificity of triplet additions can be drawn from studies of trifluoromethylcarbene[17] and dicyanocarbene.[18] In these cases, additions to *cis* olefins were not greatly nonstereospecific, but dilution with inert solvents permitted obtention of substantial triplet populations, with concomitant gross nonstereospecificity. Mention should also be made of triplet methylene, which in condensed,[19] or gas phases[20] added to *cis* olefins with marked loss of stereospecificity.

It therefore seems safe to conclude that had our cyclopentadienylidene additions involved more than a very small triplet component, substantial nonstereospecificity would have been observed.[21]

Two points require further discussion: (1) why is it not possible to increase substantially the nonstereospecificity of addition reactions of II by dilution with an inert solvent; and (2) how can we account for the 1–2% nonstereospecificity which was observed? Success of the inert diluent technique, as a method for allowing the conversion of singlet to triplet carbene, depends on the rate of singlet to triplet decay relative to the rate at which the singlet reacts with a particular substrate. Although fluorenylidene,[15] trifluoromethylcarbene,[17] and dicyanocarbene[18] can be produced as singlets in the condensed phase, and, by addition of an inert diluent, can be largely converted into the ground-state triplet species, similar experiments fail for II (see above), biscarbomethoxycarbene,[16] and methylene itself.[19] For methylene, singlet–triplet decay has not yet been observed in solution because of its high reactivity; "singlet methylene must then react on one of the first collisions with a substrate, whereas the singlet–triplet decay requires numerous inert collisions."[19] Dilution experiments with 1,2-dichlorotetrafluoroethane failed to aid the singlet–triplet transition in solution.[19,22] In the case of II, high reactivity of the singlet state may also be a significant factor in the failure to observe nonstereospecific triplet addition, even at high dilution. We have already demonstrated, on the basis of insertion and addition selectivity, that II is one of the most reactive of carbenes. Our inability to alter the highly stereospecific course of its addition reaction, even by generating the carbene in a solid olefin matrix at 77°K, is in accord with high reactivity of the singlet state. Emphasis on the reactivity of II should not obscure the fact that there may be special reasons why the rate of its singlet–triplet decay should be particularly low compared, for example, to that of fluorenylidene where the dilution experiment is successful.[15] Much remains to be learned in order to predict when the balance of rates of singlet–triplet decay and singlet olefin addition will be such as to permit obtention of triplet carbene reactions in solution. The essential failure of the dilution technique for biscarbomethoxycarbene,[16] but

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[12] A referee has suggested that, if II reacted significantly faster with the *trans* olefin than with the *cis* olefin, it would be possible for less than 1% of a *trans* impurity in the *cis* olefin to account for the observed 2–3% "nonstereospecificity." However, generation of II in a mixture of the two olefins has now shown that 4-methyl-*cis*-pentene-2 actually reacts about 10% *faster* with II than does 4-methyl-*trans*-pentene-2.

[13] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

[14] See the cautionary discussion by P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235 ff.

[15] M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4013 (1965).

[16] M. Jones, Jr., A. Kulczycki, Jr., and K. F. Hummel, *Tetrahedron Lett.*, 183 (1967); M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *ibid.*, 1391 (1967).

[17] J. H. Atherton and R. Fields, *J. Chem. Soc., C*, 1450 (1967).

[18] E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

[19] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962).

[20] For examples see R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965), and references therein; F. J. Duncan and R. J. Cvetanović, *J. Amer. Chem. Soc.*, **84**, 3593 (1962).

[21] It should be noted that tetrachloro II [E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966)] and tetraphenyl II [H. Dürr and G. Scheppers, *Ber.*, **100**, 3236 (1967)] have been generated. Tetrachloro II displays greater nonstereospecific addition tendencies than II. Addition to *cis*-butene afforded 10% *trans* product. It is interesting to note that, on the basis of its very high addition/insertion selectivity, tetrachloro II seems *less reactive* than II[5] (see below). Tetraphenyl II is reported to add to olefins only stereospecifically, but 1–2% of the nonstereospecific addition product might not have been detected by the analysis used.

[22] This experiment cannot, however, be regarded as definitive since the diluent was not inert toward methylene.

its success for dicyanocarbene,[18] seems particularly difficult to understand.

Finally, were the small nonstereospecific component of the addition reaction of II due to the coexistence of a small triplet population, we might have expected a decrease in this nonstereospecificity in the presence of 60 mol % of 2,5-dimethylhexadiene-2,4. It is known that triplet fluorenylidene reacts much more rapidly with butadiene than with *cis*-butene.[23] Triplet biscarbomethoxycarbene reacts 29 times faster with 2,3-dimethylbutadiene than with 4-methyl-*cis*-pentene 2;[16] and even triplet methylene reacts 20 times faster with butadiene than with *cis*-butene (Cvetanović).[20] It is hard to believe, therefore, that the 2% nonstereospecificity we observed stems from triplet cyclopentadienylidene. We might note that there exist no cogent theoretical or experimental results indicating that singlet carbene additions must infallibly be 100% stereospecific.[24] Alternatively, one could attribute the small nonstereospecific component of our reaction to the intervention of an excited DCPD addition reaction.

Experimental Section

Apparatus and Materials.—Ir spectra were determined on a Beckman Model 5A instrument. Nmr spectra were measured on a Varian A-60 instrument as dilute solutions in CCl_4. Uv spectra were measured on a Cary-14 instrument as pentane solutions. Preparative glpc was carried out on an Aerograph A-90 instrument, with a glass lined injector port and a 20 ft × 0.375 in. preparative SF-96 column (20% on 40–60 Chromsorb W). Injector temperature was maintained at 192°; helium pressure was 30 psig. The column temperature was 120°. Quantitative glpc analyses were carried out on a Barber–Colman, series 5000 instrument, fitted with a 100 ft, SF-96 Golay column at 120°. The injector temperature was 240°, and the nitrogen carrier gas was held at 10 psig. The flame ionization detector was calibrated with mixtures of pure products. *cis*- and *trans*-4-methyl-2-pentene were obtained from Phillips Petroleum Co. The olefins were distilled prior to use on a column packed with glass helices. Their isomeric purity was better than 99%, as determined by glpc ($AgNO_3$ column). DCPD was prepared by the method of Weil,[25] as previously discussed.[5]

Preparation of *trans*-1-Methyl-2-isopropylspiro[2.4]heptadiene-4,6 (III).—A solution of 2.00 g of DCPD in 195 g of 4-methyl-*trans*-pentene-2 was photolyzed for 1.5 hr with a 450-W Hanovia Type L lamp in a quartz immersion apparatus (Pyrex filter). The excess olefin was removed by distillation. The residue was distilled *in vacuo*, affording 2.1 g of liquid, bp 63–65° (7 torr).[26] Preparative glpc allowed collection of the major product, III. No IV (see below) was present.

Compound III showed ir, $\lambda^{\mathrm{CCl_4}}$ 3.28 (m), 3.41 (s), 6.21 (m), 6.86 (s), 7.25 (s), 7.91 (m), 8.44 (m), 8.97 (s), 9.61 (s), 9.96 (s), 11.31 (s), 13.91 (s). The uv spectrum (pentane) showed $\lambda_{\max}$ 234 mμ (ϵ 9260), 243 (sh), and 255 (sh) (ϵ 2760). The extinction at 300 mμ was 42. The nmr spectrum is described above. The estimated yield of III, based on DCPD, was 70%. *Anal.* Calcd for $C_{11}H_{16}$ (148.25): C, 89.12; H, 10.88. Found: C, 89.23; H, 11.16.

Preparation of *cis*-1-Methyl-2-isopropylspiro[2.4]heptadiene-4,6 (IV).—A similar photolysis (2.25 hr) of a solution containing 2.00 g of DCPD in 170 ml of 4-methyl-*cis*-pentene-2 afforded a residue which was distilled at 63–75° (6–8 torr) to yield 1.9 g of liquid. Preparative glpc allowed collection of the major product, IV.

Compound IV showed ir, $\lambda^{\mathrm{CCl_4}}$ 3.25 (w), 3.38 (s), 3.48 (m), 6.21 (w), 6.81 (s), 7.23 (m), 7.34 (m), 7.79 (m), 8.47 (m), 8.86 (s), 9.19 (m), 9.63 (s), 10.00 (w), 10.23 (w), 10.61 (m), 11.35 (s), 13.82 (m), 14.19 (m). The uv spectrum (pentane) showed $\lambda_{\max}$ 230 mμ (ϵ 9100), 243 (sh), and 255 (sh) (ϵ 2680). The extinction at 300 mμ was 49. The nmr spectrum is described above. The estimated yield of IV was 70%. *Anal.* Calcd for $C_{11}H_{16}$ (148.25): C, 89.12; H, 10.88. Found: C, 89.24; H, 11.14.

Compound III was also found in this reaction and was the first eluted high-boiling product. It was identified by comparison of its glpc retention time and ir spectrum with those of the authentic material. It was present to 5% of the extent of IV.

Stereospecificity of Addition of II to 4-Methyl-*cis*-pentene-2.—Into a Pyrex test tube was measured 10 ml of 4-methyl-*cis*-pentene-2 and 50 mg of DCPD. The test tube was stoppered with a serum cap, taped with black plastic tape so that only a narrow window for the admission of light remained, immersed in an ice bath, behind a Corning C.S. 3-94 filter, and irradiated for 2.5 hr with a G. E. sunlamp. Analysis by capillary glpc revealed six high-boiling products. In order of elution, these were identified as III, dicyclopentadiene (carried over from the synthesis of DCPD), an insertion product,[27] IV, and two more insertion products.[27] In two runs, with no removal of olefinic solvent, integration of the glpc areas gave the ratio III/(III + IV) as 0.012 and 0.013. In three other runs, in which most of the olefin was removed by distillation prior to analysis, the ratio was higher, 0.015. Each analysis was based on five glpc traces. The average deviation was better than 5%.

It was shown that III and IV did not crack or isomerize under analytical conditions. Photolysis, as above, of pure IV (29 mg in 10 ml of cyclohexane) in the presence of DCPD did not result in the formation of III.

Injection of a solution of 50 mg of DCPD in 10 ml of 4-methyl-*cis*-pentene-2 into the Barber–Colman glpc instrument afforded a chromatogram on which III/(III + IV) was 0.277.

Thermolysis at 180° of 50 mg of DCPD in 10 ml of the *cis* olefin afforded a product mixture in which III/(III + IV) was 0.044.

An aliquot of a solution of 50 mg of DCPD in the *cis* olefin was placed in an nmr tube. The tube was cooled to 77°K in a special nitrogen dewar flask fitted with a quartz probe. Photolysis, using the C.S. 3-94 filter, was carried out for 30 min; the contents of the nmr tube were thawed (in the dark), refrozen, and again irradiated. After 4.25 hr of this cyclical procedure, an ir spectrum revealed the absence of DCPD, and glpc gave III/(III + IV) as 0.025.

Dilution Experiments. A.—Hexafluorobenzene (Aldrich Chemical Co.) was added in a known amount to the *cis* olefin so as to make a total volume of 10 ml. DCPD (50 mg) was added, and photolysis was carried out in Pyrex test tubes as described above. Samples were concentrated by distillation, and the residues were analyzed by capillary glpc. The results appear in Table I.

B.—Octafluorocyclobutane (Matheson Co.) and the *cis* olefin together with 25 mg of DCPD were sealed into a screw-top Carius tube (Fisher–Porter Co.). The solution volume was *ca.* 10 ml. Photolysis was carried out as previously. The diluent was allowed to evaporate and the residue was analyzed. The results appear in Table II.

C.—Acrylonitrile (Matheson Coleman and Bell Co.) and the *cis* olefin were mixed in known proportion with 50 mg of DCPD in a Pyrex test tube. The solution volume was 10 ml. After the usual photolysis, the samples were concentrated by distillation and analyzed. The results appear in Table III.

D.—The results of dilution experiments with 2,5-dimethylhexadiene-2,4 are described above. The procedure was as described for C.

Photoisomerization of III and IV was investigated by preparing solutions of the pure compounds (100 μl in 10 ml of *n*-hexane) and irradiating these in a quartz flask, under a nitrogen atmosphere, with 2537 Å light in a Rayonet, Srinivasan-Griffen reactor. At intervals, aliquots were removed and analyzed by capillary glpc. The loss of spiro[2.4]heptadiene product was followed relative to an internal *n*-decane standard. The final results of these experiments appear above.

Several further control experiments are described at the end of the Results.

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[23] M. Jones, Jr., and K. R. Rettig, *J. Amer. Chem. Soc.*, **87**, 4015 (1965).

[24] It has, for example, been argued that observation of nonstereospecific addition is not inconsistent with a singlet carbene intermediate. See ref 14 and W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

[25] T. Weil and M. Cais, *J. Org. Chem.*, **28**, 2472 (1963).

[26] Boiling points are uncorrected.

[27] These products are assumed to be insertion products, since such products have been previously shown to accompany the addition reactions of II.[5]

Registry No.—III, 17392-80-2; IV, 17392-81-3; cyclopentadienylidene, 1729-01-5; 4-methyl-*cis*-pentene-2, 691-38-3; hexafluorobenzene, 392-56-3; octafluorocyclobutane, 115-25-3; acrylonitrile, 107-13-1.

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The Composition of Grignard Compounds. V. In Triethylamine Solution

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For the first time Grignard compounds have been prepared directly in triethylamine solvent. In some cases side reactions occur during the preparation in triethylamine (quaternary salt formation and dehydrohalogenation); however, the reaction readily produces the desired product in 50–90% yield. The lower solubility of the Grignard compounds in triethylamine (0.1–0.9 *m*) as compared to diethyl ether (2–4 *m*) limits somewhat the useful concentration range in which the reagent can be employed. Nevertheless, reaction of the material with a carbonyl compound proceeds smoothly and results in a ratio of addition to reduction product that is significantly lower than that found when the reagent is prepared and reacted in diethyl ether. The composition of Grignard compounds in tertiary amine solvent was shown to be best represented by the equilibrium $R_2Mg + MgX_2 \rightleftarrows 2RMgX$. This equilibrium was shown to lie almost completely to the right when X = Cl and Br but not nearly so much to the right when X = I. The redistribution of $(CH_3)_2Mg$ and $(C_2H_5)_2Mg$ with $MgBr_2$ and MgI_2 was shown to take place readily in triethylamine and as the tetramethylethylenediamine complexes in diethyl ether and benzene.

The preparation of Grignard reagents in ether solvents and the reaction of these compounds with various organic functional groups have been known to chemists for decades. However, it is only recently that the composition of this highly useful reagent has been elucidated. The controversy surrounding the composition problem, coupled with the reagent's popularity for organic syntheses, have resulted in the accumulation of a great deal of data concerning, directly or indirectly, the Grignard reagent in ether solvents.[3] In addition, recent effort has been directed toward the discovery of new solvents, particularly nitrogen-containing solvents, that might function in place of ethers for the preparation and reaction of Grignard compounds; hexamethylphosphoramide[4] and disubstituted amides[4b] have been investigated for this purpose. Surprisingly, little effort has been directed toward the use of pure amine solvents for Grignard compounds[5] although tertiary amines, substituted amides, and nitrogen heterocycles have been used in stoichiometric amounts for the preparation and/or reaction in ether[6] and hydrocarbon[7] diluents. Some reactions in nitrogen-containing solvents have been studied with Grignard compounds that were just prepared in diethyl ether which was subsequently displaced with the secondary solvent.[8] This method of preparation was used to obtain ethylmagnesium bromide triethylaminate which was then crystallized for the only reported structural study[9] of Grignard compounds complexed to an amine.

The scant information available gives little indication of either the consequences of using an amine rather than an ether solvent for the direct preparation and reaction of Grignard reagents or the reagent's composition when prepared directly in amine solution. This lack of information, as well as our continued interests in the composition of Grignard compounds in various solvents, prompted this study with triethylamine, the nitrogen analog of diethyl ether. The synthetic aspects will be considered first, followed by a presentation of the evidence pertaining to the composition of Grignard reagents in amine solvents.

Results and Discussion

Examination of Table I reveals that the preparation of Grignard reagents in triethylamine suffers some limitations compared to diethyl ether or tetrahydrofuran as a solvent. The yields for the ethylmagnesium halides are reasonably high but decrease for the *sec*-butyl-, *t*-butyl-, and phenylmagnesium halides. The yields are highest for the alkylmagnesium chlorides but generally show a decrease for the bromides and iodides. Although dehydrohalogenation of the alkyl halide by triethylamine appears to be a very minor reaction even with the *t*-butyl halides, quaternary salt formation can be more serious. Since quaternary salt formation increases in the order *t*-alkyl < *sec*-alkyl < *n*-alkyl and Cl < Br < I, alkyl halides such as ethyl iodide must have minimum contact with the tertiary amine prior to reaction.

Perhaps the most notable feature of triethylamine as a solvent for Grignard compounds is the low solubility of some of the compounds in this solvent. Whereas Grignard compounds in diethyl ether usually have a solubility in the range 2–4 *m*, in triethylamine the solubility for the compounds investigated range from

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(3) (a) E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967); (b) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966); (c) R. M. Salinger in "Survey of Progress in Chemistry," Vol. 1, A. F. Scott, Ed., Academic Press, Inc., New York, N. Y., 1963, pp 301–324; (d) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Inc., Englewood Cliffs, N. J., 1954.

(4) (a) G. Fraensel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965); (b) H. Normant, *Bull. Soc. Chim. Fr.*, 1434 (1963); (c) J. Fauvarque and J. F. Fauvarque, *C. R. Acad. Sci., Paris*, **263**, 488 (1966).

(5) Reference 3d, p 49.

(6) (a) F. Drahowyal, *Monatsh. Chem.*, **82**, 794 (1951); (b) F. Drahowyal and H. Konig, *ibid.*, **85**, 654 (1954).

(7) (a) E. C. Ashby and R. Reed, *J. Org. Chem.*, **31**, 985 (1966); (b) ref 3d, p 50.

(8) A. Kirmann and J. Robesiaka, *Bull. Soc. Chim. Fr.*, 2370 (1967).

(9) J. Torey and G. D. Stucky, *Chem. Commun.*, 1168 (1967).