**Ethyl (−)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate.**—The procedure as described in an earlier publication[6] was utilized to yield the N-nitrosocarbamate as a yellow oil, $[\alpha]^{25}$D −251° (*c* 7.4, ether). This material was homogeneous as shown by tlc (pentane–ether eluent) and had identical ir and nmr spectra with those reported.[3] The racemic material was prepared in an identical manner.

**Decomposition of Ethyl (±)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in Cyclohexane–Cyclohexene and Benzene–Cyclohexene Mixtures. Determination of Spiropentane/Allene Ratios.**—A 47.8-ml, magnetically stirred, water-jacketed, volumetric reaction flask connected to a pressure-compensated gas buret and a constant-temperature circulator at 30.0° was thoroughly flushed with dry nitrogen. After addition of 0.0620 g (0.20 mmole) of the N-nitrosocarbamate and the appropriate solvent mixture, a 0.38-ml (0.20 mmole) portion of 5.6 *M* sodium methoxide in methanol was added. The reaction was allowed to continue until nitrogen evolution was complete; this normally required 3 hr and gave 80–100% gas evolution. The mixture was then analyzed by glpc using the 600-D instrument with a $^1/_8$ in. × 6 ft column packed with 10% SE 30 on 60–80 mesh Chrom W with DMCS at 156° with temperature programming for elution of the spiropentane. In each case the chromatogram showed no components in addition to the standard, allene, and spiropentane (<1% detectable) with the exception of reactions in which cyclohexane was the solvent. In pure cyclohexane 2.6% of another component was observed, and the amount of this material observed was proportionate to the amount of cyclohexane used in the reactions.

**Decomposition of Ethyl (−)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in Various Solvents. Determination of the Optical Rotation of the 1,3-Diphenylallene.**—A procedure identical with that for the determination of spiropentane to allene ratios was utilized except that the (−)-N-nitrosocarbamate, $[\alpha]^{25}$D −251° (*c* 7.4, ether), was used. After the reaction was complete (nitrogen evolution ceased) the reaction mixtures from the cyclohexane and benzene reactions were poured into equal volumes of cyclohexene, and the reaction mixtures from reactions in cyclohexene, methanol, and *t*-butyl alcohol were poured into equal volumes of cyclohexane. These mixtures were evaporated *in vacuo* to an oil, which was immediately chromatographed over 10 g of silica (hexane eluent). The resulting chromatography fractions which were shown to contain only 1,3-diphenylallene by glpc were then used for specific rotation determination. The concentration of the allene in these fractions was determined by glpc by comparison to a standard of approximately equal concentration using the 600-D instrument with a $^1/_8$ in. × 6 ft column packed with 10% SE 30 on 60–80 mesh Chrom W with DMCS at 156°. Using this procedure the specific rotation (+30°) of the (+)-1,3-diphenylallene was obtained for identical reactions in the following solvents: cyclohexene, 683°; cyclohexane, 686°; benzene, 607°; *t*-butyl alcohol, 350°; methanol, 197. Control experiments showed (+)-1,3-diphenylallene to be optically stable when exposed to sodium methoxide in the above solvents at comparable concentrations and exposure times.

**Determination of Relative Solvent Polarities.**—The procedure of Berson, Hamlet, and Mueller[8] was used. In a nitrogen-flushed, water-jacketed flask kept at 30.0° by use of a constant-temperature circulator was placed 30 ml of the appropriate solvent and 1.3 ml of freshly distilled methyl acrylate. A freshly distilled 1.3-ml portion of cyclopentadiene was then added by use of a syringe through a rubber septum. The reaction mixture was allowed to stir for 24 hr and then evaporated to an oil by use of a rotary evaporator at room temperature. A small portion of ether was added to the oil and again the solvent was removed. Ether was added to the resulting oil and this solution was analyzed by glpc on the 600-D instrument using a $^1/_8$ in. × 10 ft column packed with TCEP on 60–80 mesh Chrom W with DMCS and a nitrogen pressure of 24 psig at 103°. The following *endo*/*exo* ratios (±2%) were obtained for the solvents listed: acetone, 0.414; benzene, 0.497; cyclohexene, 0.506; hexane, 0.577; cyclohexane, 0.595. Control experiments for reaction time and work-up procedure did not alter the observed ratios.

**(+)-*trans*-1,2-Diphenyl-1′,2′-tetramethylenespiropentane.**—To a solution of 1.54 g (4.98 mmoles) of ethyl (+)-N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate, $[\alpha]^{25}$D +210° (*c* 5.8, ether), in 100 ml of cyclohexene at 22° was added 1.035 ml (5.96 mmoles) of a 5.79 *M* solution of sodium methoxide in methanol. After gas evolution was complete (1 hr), analysis of an aliquot of the reaction mixture by glpc on the 600-D instrument with a $^1/_8$ in. × 5 ft column packed with 6% apiezon L on 60–80 mesh Gas-Chrom Z at 233° and an inlet pressure of 30 psig showed a 26% yield of the spiropentane. After addition of 150 ml of heptane to the reaction mixture and evaporation *in vacuo* to a volume of approximately 60 ml, the mixture was chromatographed over 220 g of silica (hexane eluent). Incomplete separation was obtained as glpc analysis of the chromatography fractions showed elution of the allene, followed by fractions containing both allene and spiropentane, then followed by fractions containing only the spiropentane. These latter fractions were combined and evaporated to an oil. Crystallization of this oil from 95% ethanol at −78° gave 66 mg of the spiropentane: $[\alpha]$D$^{25}$ +135° (*c* 19.54, hexane); mp 97–97.5°; infrared, $\lambda_{\max}^{\mathrm{KBr}}$ 1600, 750, and 700 cm$^{-1}$ (phenyls); nmr, $\tau$ 2.85 (m) ten phenyls, 7.67 (pair of doublets, 3.8 cps) two hydrogens of spiropentane adjacent to phenyls, 8.0–9.2 (m) ten remaining protons; mass spectrum, *m/e* 274 (parent peak), 192, 191, 183, 141, 115, and 91; ultraviolet, $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 238 m$\mu$ (log $\epsilon$ 4.2), $\lambda_{\mathrm{sh}}^{95\%\ \mathrm{EtOH}}$ 268 m$\mu$ (log $\epsilon$ 3.2), 275 m$\mu$ (log $\epsilon$ 3.0).

*Anal.* Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.65; H, 8.07.

**1-Methoxy-*trans*-2,3-diphenylcyclopropane.**—To a solution of 1.65 g (5.32 mmoles) of ethyl (±)-N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in 200 ml of anhydrous methanol was added 1.0 ml (5.6 mmoles) of a 5.6 *M* solution of sodium methoxide in methanol. Gas was rapidly and vigorously evolved. After gas evolution was complete, glpc of the reaction mixture showed the presence of only two components, 1,3-diphenylallene (67%) and 1-methoxy-*trans*-2,3-diphenylcyclopropane (33%). Evaporation of the reaction mixture to a volume of 30 ml and separation of the second component by preparative glpc on the A-350-B instrument with a 0.5 in. × 6 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 190° and an inlet pressure of 50 psig gave the ether as a white solid: mp 60–62°; infrared, $\lambda_{\max}^{\mathrm{KBr}}$ 1600, 750, 700 (phenyls), 1110 cm$^{-1}$ (ether); nmr, $\tau$2.83 (m) ten phenyls, 6.42 (q) one hydrogen of cyclopropane adjacent to methoxy group, 6.81 (s) three methyls, 7.57 (m) two hydrogens of cyclopropane adjacent to phenyls; mass spectrum, *m/e* 224 (base and parent peak), 209, 193, 192, 147, and 77.

*Anal.* Calcd for $C_{16}H_{16}O$: C, 85.67; 7.19. Found: C, 85.58; H, 7.10.

**Registry No.**—Cyclopropylidene, 2143-70-6; allene, 463-49-0; spiropentane, 157-40-4; (+)-*trans*-1,2-diphenyl-1′,2′-tetramethylenespiropentane, 19817-59-5; 1-methoxy-*trans*-2,3-diphenylcyclopropane, 19817-60-8.

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# Stereoselectivity of Carbene Intermediates. VI. Selectivity of Phenylchlorocarbene[1]

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At least formally, phenylhalocarbenes can be generated by the action of base on benzal halides **1**,[4] or by photoinduced elimination of nitrogen from phenyl-

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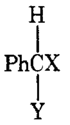
[1] Part V: R. A. Moss and J. R. Przybyla, *Tetrahedron*, **25**, 647 (1969).

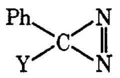
[2] National Science Foundation Summer Undergraduate Research Participant, 1968 (GY-4154).

[3] Henry Rutgers Fellow, 1968–1969.

[4] See R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962), for example.



**1a**, X = Br; Y = F
**b**, X = Y = Cl
**c**, X = Y = Br



**2a**, Y = Cl
**b**, Y = Br

halodiazirines **2**.[5] Our recent studies of phenylfluorocarbene (Ph–C–F)[1] and phenylbromocarbene (Ph–C–Br)[5,6] have raised two significant questions which are answerable by a selectivity study of phenylchlorocarbene (Ph–C–Cl). (1) As generated by the action of potassium *t*-butoxide on **1c** or of light on **2b**, "Ph–C–Br" exhibits nonidentical abilities to discriminate between different olefins.[5,6] The discrepancy has been attributed to the intervention of a carbene–base complex (carbenoid) in the butoxide-induced reaction. In view of the supposed superiority of Cl over Br in stabilizing a divalent carbon center,[7] would the butoxide-induced decomposition of **1b** lead to a "free" Ph–C–Cl, identical with that generated by photolysis of **2a**? (2) Ph–C–Br and Ph–C–F, as generated from benzal halides **1c** and **1a**, showed a relatively small difference in their abilities to discriminate between members of a standard set of olefinic substrates.[1] If, however, these base-catalyzed carbene generations both involved carbenoids rather than free carbenes, then the halogen–divalent carbon resonance interaction, which is believed to confer stability (and selectivity) on a carbene,[7] must have been absent or, at best, reduced. Would a selectivity comparison of *photolytically generated* (uncomplexed) phenylhalocarbenes uncover large differences in discrimination between the phenylhalocarbenes as a function of halogen atom identity?

Ph–C–Cl was generated from **1b** by the action of potassium *t*-butoxide[8] at 25°, and added to tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, and *trans*-butene. The product cyclopropanes were identified by comparison of their nmr spectra with reported data.[9] The same product cyclopropanes were obtained in good yield when dilute olefinic solutions of phenylchlorodiazirine[10] were irradiated with a G. E. sunlamp at *ca.* 25° (Pyrex filter).

In all cases, for both generative methods, the alkyl regions of nmr spectra of the crude products were sufficiently clean and compatible so that the nmr spectra of the cyclopropane *mixtures*, formed by generation of Ph–C–Cl in selected binary mixtures of the olefins, could be used to determine quantitatively the cyclopropane mixture compositions. (The nmr analyses were similar to those employed in our Ph–C–Br studies,[5,6] and are detailed in the Experimental Section.) We were thus able to determine the relative rates of addition of base- and light-generated Ph-C-Cl to the several olefins. The *experimental* rates are collected in Table I. Control experiments, using prepared mixtures of pure products, demonstrated the accuracy of the nmr analyses, and also the constancy of product ratios to all experimental conditions. Table II contains the data of Table I, normalized to an isobutene standard. Analogous data for Ph–C–Br and Ph–C–F have also been included in Table II for purposes of comparison. Attempts in this laboratory to prepare a suitable precursor for the photolytic generation of Ph–C–F have met with failure.

TABLE I

EXPERIMENTAL RELATIVE RATES OF ADDITION OF PHENYLCHLOROCARBENE TO SELECTED OLEFINS, *ca.* 25°

| Case | Olefin A/olefin B | $(k_A/k_B)_{\text{base}}$[a] | $(k_A/k_B)_{\text{light}}$[b] |
|---|---|---|---|
| 1 | Isobutene/ tetramethylethylene | 0.38 (3.93)[c] | 0.20 (6.56)[c] |
| 2 | Trimethylethylene[d]/ tetramethylethylene | 0.60 (7.93) | 0.62 (12.6) |
| 3 | *trans*-Butene/ tetramethylethylene | 0.042 (3.63) | 0.039 (10.4) |
| 4 | Isobutene/ *cis*-butene[d] | 3.2 (3.23) | 2.7 (8.24) |

[a] Ph–C–Cl from benzal chloride and potassium *t*-butoxide. [b] Ph–C–Cl from photolysis of phenylchlorodiazirine. [c] Numbers in parentheses refer to the per cent average deviation of *n* experiments. [d] These rates are composites of both stereochemical modes of addition of Ph–C–Cl to these olefins.

The data of Table I reveal similarity but not identity of the base- and light-generated Ph–C–Cl species. In cases 2 and 3, the experimentally observed relative addition rates of both species are the same, within experimental error. In case 4, the difference lies just outside the combined experimental error. Moreover, as detailed in the Experimental Section, the stereoselectivity of Ph–C–Cl additions to *cis*-butene and trimethylethylene was essentially *independent* of generative method. There can be no question, however, that the experimental difference observed in case 1 is real. It is interesting to note that in the Ph–C–Br studies,[5,6] where *all* olefin pairs examined revealed selectivity differences between the base- and light-produced Ph–C–Br, it was this same tetramethylethylene–isobutene pair which revealed much of the largest difference.

A simple rationale, which is in accord with the facts but not exclusively demanded by them, is that a carbene–base complex (carbenoid) is at least partly involved in the benzal chloride–potassium *t*-butoxide reactions, whereas a free carbene is involved in the phenylchlorodiazirine photolyses.[11] Though one can speculate, it is not yet clear why the selectivity differences show up so dramatically in case 1 (Table I), or whether mechanistic significance can be attached to the substantial identity of all other selectivity measurements we have been able to make on base- and light-generated Ph–C–Cl species.

With regard to the over-all selectivity of the various carbenic species (Table II), the data show (1) Ph–C–X produced from benzal halides and potassium *t*-butoxide show only small variations in selectivity as a function of X; (2) Ph–C–X photogenerated from phenylhalodiazirines show, at most, only a marginally greater selectivity for X = Cl, as opposed to X = Br. Synthetic difficulties attend attempted generation of Ph–C–F by photolytic means. Based on the fore-

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(5) R. A. Moss, *Tetrahedron Lett.*, 4905 (1967).

(6) R. A. Moss and R. Gerstl, *Tetrahedron*, **22**, 2637 (1966).

(7) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 36 ff.

(8) Alfa Inorganics, Inc. Other commercially available reagents lead to unacceptably slow reaction at 25°. We thank Professor G. L. Closs for this information.

(9) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

(10) W. H. Graham, *J. Amer. Chem. Soc.*, **87**, 4396 (1965). We thank Dr. Graham for detailed instructions for this preparation.

(11) Explanations involving different multiplicities for the base- and light-generated Ph–C–Cl species seem precluded, since both add stereospecifically to *cis*- and *trans*-butene.

TABLE II

KINETIC SELECTIVITY OF PHENYLHALOCARBENES, *ca.* 25°

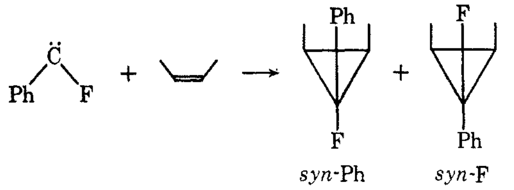
| | Relative rates of addition | | | | |
|---|---|---|---|---|---|
| | Ph-C-Br | | Ph-C-Cl | | Ph-C-F |
| Olefin | Base[a] | Light[b] | Base[c] | Light[c] | Base[d] |
| Tetramethylethylene | 1.6 | 4.4 | 2.6 | 5.1 | 2.7 |
| Trimethylethylene[e] | 1.3 | 2.5 | 1.6 | 3.2 | 1.2 |
| Isobutene | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| *cis*-Butene[e] | 0.29 | 0.53 | 0.31 | 0.37 | 0.12 |
| *trans*-Butene | 0.15 | 0.25 | 0.11 | 0.20 | 0.10 |
| "Spread"[f] | 11 | 18 | 24 | 25 | 27 |

[a] Reference 6. [b] Reference 5. [c] This work. [d] Reference 1. [e] These rates are composites of both stereochemical modes of addition of Ph–C–X to these olefins. [f] Ratio of fastest to slowest addition rate.

going, however, it seems likely that the selectivity of this species will be very similar to that of the base-generated Ph–C–F.

As specific answers to the two questions posed above, we conclude (1) photo- and base-generated Ph–C–X do not become wholly identical upon change of X from Br to Cl. The base-induced reactions, in both cases, are probably best regarded as involving carbene–base complexes or carbenoids; (2) the phenylhalocarbenes do not show large selectivity differences as a function of halogen no matter how they are generated. In this respect, they resemble the monohalocarbenes. Only in the case of the dihalocarbenes has it been shown that halogen variation can result in reasonably large selectivity variation.[12]

We also investigated the possibility of predicting the stereoselectivity of a carbene olefin addition reaction. Consider reaction 1, the addition of Ph–C–F to *cis*-butene.[1] Can the observed, kinetically controlled, *syn*-F/*syn*-Ph ratio be predicted from an equation such as eq 2, using analogous stereoselectivity data for Ph–C–Cl and F–C–Cl? To answer this question, we redetermined stereoselectivity data for F–C–Cl[12] with *cis*-butene and trimethylethylene substrates at 25°. We also redetermined such stereoselectivity data for Ph–C–Cl[9] at 25°. Details appear in the Experimental Section. The data, in the form of eq 2, together with *observed* and *predicted* Ph–C–F stereoselectivity, are summarized in Table III.[13,14]



(1)

$$\left(\frac{syn\text{-F}}{syn\text{-Cl}}\right)_{\text{F-C-Cl}} \left(\frac{syn\text{-Cl}}{syn\text{-Ph}}\right)_{\text{Ph-C-Cl}} = \left(\frac{syn\text{-F}}{syn\text{-Ph}}\right)_{\text{Ph-C-F}} \quad (2)$$

TABLE III

PREDICTED STEREOSELECTIVITY OF PHENYLFLUOROCARBENE, 25°

| Olefin | $\left(\frac{syn\text{-F}}{syn\text{-Cl}}\right)_{\text{F-C-Cl}}$ | $\left(\frac{syn\text{-Cl}}{syn\text{-Ph}}\right)_{\text{Ph-C-Cl}}$ | $\left(\frac{syn\text{-F}}{syn\text{-Ph}}\right)_{\text{Ph-C-F}}$ Predicted | Observed |
|---|---|---|---|---|
| *cis*-Butene | 0.42 | 2.10 | 0.88 | 1.23[a] |
| Trimethylethylene | 0.46 | 1.18 | 0.54 | 0.76[a] |

[a] Data of ref 1.

Although the predicted *syn*-F/*syn*-Ph ratios change in the proper direction upon change of the olefin from *cis*-butene to trimethylethylene, the predicted ratios are both too small.

Carbene stereoselectivity arises in differential nonbonded interactions between carbene substituents and olefinic substituents. The strength of these interactions and therefore the resultant stereoselectivity will be dependent on the separation and orientation of the carbene and olefin at the transition state for the addition reaction. Therefore eq 2 should hold most closely for carbenes of similar kinetic selectivities, in which, presumably, the addition reaction transition states are similarly located along the reaction coordinate. F–C–Cl is about ten times more selective than either Ph–C–Cl or Ph–C–F,[1] however, and the transition states of its olefin addition reactions are likely to be considerably "tighter" than those of the other two carbenes. It is not unreasonable to suggest that, if the F–C–Cl addition transition states were somewhat "looser," then the effects of the differential polarizabilities of Cl and F (which are believed to determine mainly the stereoselectivity of F–C–Cl[12,15]) would be mitigated; the *syn*-F/*syn*-Cl ratios would increase; and the predicted *syn*-F/*syn*-Ph ratios would more closely approach the observed values.

## Experimental Section

**1-Phenyl-1-chlorocyclopropanes.**—The adducts of phenylchlorocarbene and tetramethylethylene (Chemical Samples Co.), trimethylethylene (Aldrich), isobutene, and *cis*-butene (Matheson) were prepared in the following general way. Benzal chloride (Eastman), 1 equiv, was added to 10 equiv of the indicated olefin in a screw-top Carius tube (Fisher-Porter Co.) at −70°. Potassium *t*-butoxide (Alfa Inorganics), 1.4 equiv, was added. The tube was sealed, secured to a rotary mixer, and agitated for 2 days at *ca.* 25°. The contents of the tube were then washed three times with water, and once with a saturated $NaHCO_3$ solution. The resulting organic phase was dried over $CaCl_2$. Excess olefin was removed with a rotary evaporator and the resultant cyclopropane was purified by vacuum distillation.

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(12) R. A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967); see, also, the discussion in ref 1.

(13) In the light of $CCl_2$ studies,[14] CFCl may well be a free carbene, even when base generated. It would be best, therefore, to use stereoselectivity data for light-generated (free) Ph–C–X in Table III. Such data are not available for Ph–C–F. In view of the identity (within experimental error) of stereoselectivity data for base- and light-generated Ph–C–Cl (and the great similarity of the analogous Ph-C-Br data[5]) it seems reasonable to use stereoselectivity data for base- and light-generated Ph–C–X interchangeably in eq 2 and Table III.

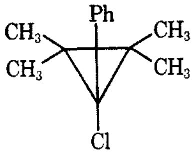
(14) Several thermal α-elimination reactions lead to the same $CCl_2$ species: D. Seyferth, M. E. Gordon, J. Y-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967); O. M. Nefedov and R. N. Shafran, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 538 (1965). Photolysis of 1,1-dichloro-2-phenylcyclopropane may lead to the same intermediate: M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Waller, *J. Amer. Chem. Soc.*, **88**, 3167 (1966).

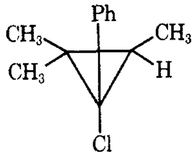
(15) R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

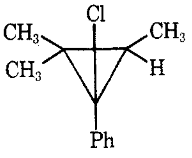
Products were identified by comparison of their nmr spectra with the reported data.[9] Yields were somewhat lower than in the literature method, which employed higher reaction temperatures.[9]

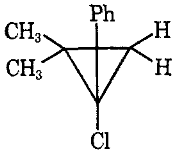
1-Phenyl-1-chloro-2,3-*trans*-dimethylcyclopropane was prepared by photolyzing a solution of 0.99 g of phenylchlorodiazirine[10] in 22 g of *trans*-butene (Matheson) in the Carius tube with a G. E. sunlamp for 3 hr at 22°. Removal of olefin, followed by distillation of the residue at 54–56° (0.6 torr), afforded 0.78 g (66%) of product having the correct nmr spectrum.[9]

**Nmr Analyses.**—Binary mixtures of the five products, **3–7**, were quantitatively analyzed.


**3**


**4a**


**4b**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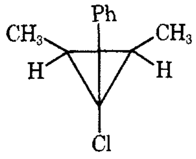
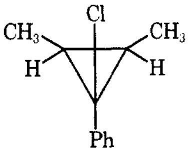
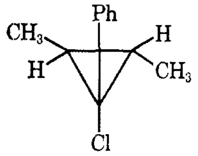

**6a**


**6b**


**7**

**Case** (1), **3** + (**4a** + **4b**).—Cyclopropane **3** shows a singlet at 62.5 cps,[16] worth six protons (methyls *syn* to Ph). Cyclopropanes (**4a** + **4b**) show *inter alia* absorptions at 48, 55, and 64 cps. The 48-cps absorption represents the *syn*-Ph methyl group of **4b**. From examination of spectra of synthetic (**4a** + **4b**), the integral ratio (55 + 64)/48 was found to be 1.58. The ratio **4b**/**4a** was determined to be 1.18 (see below). With these data, and by integration of the regions 46–50 (area 1) and 52–66 cps (area 2) in the **3** + **4** mixture, it can be deduced that

$$\frac{(\mathbf{4a} + \mathbf{4b})}{\mathbf{3}} = \frac{3.72(\text{area 1})}{(\text{area 2}) - 1.58(\text{area 1})}$$

Using this expression, four prepared mixtures of **3** and (**4a** + **4b**) were analyzed with an average error of 6.7%.

**Case** (2), **3** + **5**.—Cyclopropane **5** shows absorptions at 47 cps (methyl *syn* to Ph) and at 60 and 66 cps (H *syn* to Ph). In the **3** + **5** mixture, the regions 45–49 (area 1) and 58–68 cps (area 2, which includes the six-proton **3** absorption at 62.5 cps) are integrated. With these data and the **5** assignments (above) it can be shown that

$$\frac{\mathbf{5}}{\mathbf{3}} = \frac{2(\text{area 1})}{(\text{area 2}) - 0.33(\text{area 1})}$$

Using this expression, three prepared mixtures of **3** and **5** were analyzed with an average error of 3.8%.

**Case** (3), **5** + (**6a** + **6b**).—Cyclopropane **5** shows absorptions at 47 cps (methyl *syn* to Ph), and at 60, 66, 74, and 80 cps (ring protons, AB system, value two protons). Cyclopropanes (**6a** + **6b**) show absorptions at *ca.* 58 cps (methyls of **6a**) and at *ca.* 76 cps (all protons of **6b**[6,9]). It is known that the area ratio 47/(60 + 66 + 74 + 80) in **5** is 0.67, and that the ratio **6b**/**6a** = 2.10 (see below). With this, and with integration, in the **5** + (**6a** + **6b**) mixture, of the regions 45–49 (area 1) and 56–82 cps (area 2), it can be shown that

$$\frac{\mathbf{5}}{(\mathbf{6a} + \mathbf{6b})} = \frac{2.45(\text{area 1})}{(\text{area 2}) - 0.67(\text{area 1})}$$

Using this expression, three prepared mixtures of **5** + (**6a** + **6b**) were analyzed with an average error of 4.1%.

**Case** (4), **3** + **7**.—The nmr spectrum of pure **7** was divided into two regions, 42.5 – 57 cps (area 2) and 57–69 cps (area 1). The integral ratio (area 1)/(area 2) was found to be 0.37. Area 2 represents the three protons of the methyl *syn* to Ph in **7**. Remembering that **3** exhibits a six-proton singlet at 62.5 cps, determination of the integral ratio of the two regions defined above in the **3** + **7** mixture leads to

$$\frac{\mathbf{7}}{\mathbf{3}} = \frac{2.0(\text{area 2})}{(\text{area 1}) - 0.37(\text{area 2})}$$

Using this expression, six prepared mixtures of **3** + **7** were analyzed with an average error of 8.0%.

**Relative Rate Experiments.**—The benzal chloride experiments involved 0.5 g (3.11 mmol) of benzal chloride and 0.5 g (4.46 mmol) of potassium *t*-butoxide. These reagents were added to a mixture of olefins A and B (each carefully weighed) in a Carius tube at −70°. The olefins were each present in at least tenfold excess over the benzal chloride. The tube was sealed and warmed to room temperature. The remainder of the procedure was as described above. After removal of excess olefin on the rotary evaporator, the cyclopropane product ratio was determined by nmr. The relatives rates of the carbene addition to olefins A and B were then calculated in the usual manner. Control experiments demonstrated the constancy of products ratios under resubmission of the products to experimental conditions, and also after extended periods on the rotary evaporator.

In phenylchlorodiazirine experiments, weighed amounts of olefins A and B were condensed into the Carius tube and 100 mg of phenylchlorodiazirine was added. The tube was sealed, warmed to room temperature, and irradiated for 1 hr with a G. E. sunlamp (Pyrex filter). A running-water bath maintained the temperature at *ca.* 24–26°. After photolysis, the tube was cooled to −70° and opened. Warming caused excess olefin to evaporate. The residue was stripped (if necessary) of higher boiling olefins, taken up in $CCl_4$, and analyzed by nmr. Control experiments demonstrated the constancy of product ratios to photolytic and work-up conditions. Data for all relative rate experiments are collected in Table I.

**Stereoselectivity of Ph–C–Cl.**—Generation of Ph–C–Cl in trimethylethylene led to **4a** + **4b**, whereas its generation in *cis*-butene led to **6a** + **6b**. These mixtures were analyzed by nmr spectroscopy.[9] For Ph–C–Cl generated by the action of potassium *t*-butoxide on benzal chloride, **4b**/**4a** was 1.27, 1.22, 1.04, and 1.19 in four experiments with trimethylethylene (25°). Over three experiments with *cis*-butene, **6b**/**6a** was 1.96, 2.03, and 2.30. For Ph–C–Cl generated by photolysis of phenylchlorodiazirine (25°) the corresponding data were trimethylethylene, 1.35, 1.26, 1.21, 1.28; *cis*-butene, 1.91, 1.95, and 2.06.

**Stereoselectivity of F–C–Cl.**—Addition of F–C–Cl, produced by the action of potassium *t*-butoxide on *sym*-difluorotetrachloroacetone, to trimethylethylene and *cis*-butene afforded sets of isomers with the distributions summarized in Table III. Analyses were by $^{19}F$ nmr spectroscopy.[15] The trimethylethylene experiment was easily carried out at 25° in the manner already described.[15] Results were *syn*-Cl/*syn*-F = 2.22 and 2.18. The addition of F–C–Cl to *cis*-butene at 25° was accomplished as follows. *sym*-Difluorotetrachloroacetone (Allied Chemical Co.) (4.02 g, 0.035 mol) was *sealed* into a small ampoule. The ampoule was placed in an 18-in. Carius tube. The tube was cooled to −70°, and 43 g (0.77 mol) of *cis*-butene was condensed into it. Then, 4.66 g (0.042 mol) of potassium *t*-butoxide was added. The tube was sealed and warmed to 25°. Shaking the pressure tube ruptured the vial contained within it and initiated the reaction, which was then continued by securing the pressure tube to the rotary mixer for 2 hr. Work-up and analysis of the fluorochlorocyclopropane isomers could then be carried out as previously described.[15] Results for two experiments were *syn*-Cl/*syn*-F = 2.34 and 2.45.

**Registry No.**—Phenylchlorocarbene, 19807-41-1; phenylbromocarbene, 14541-26-5; phenylfluorocarbene, 17825-75-1; **3**, 3141-40-0; **4a**, 13153-95-2; **4b**, 13153-96-3; **5**, 19817-55-1; **6a**, 13153-99-6; **6b**, 13154-00-2; **7**, 19817-58-4.

**Acknowledgments.**—$^{19}F$ nmr spectra were determined by Dr. L. A. Wilson of Varian Associates, to whom we are most grateful. Financial support by

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[16] All nmr spectra were determined in $CCl_4$ solution with a Varian A-60 spectrometer. Chemical shifts are reported in cycles per second downfield from internal TMS. Peaks will be designated by their chemical shift positions.

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## A Study of the Enolization of the *syn* and *anti* Photodimers of 1,4-Naphthoquinone

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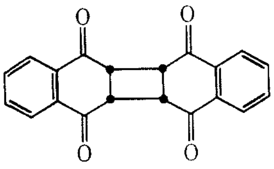
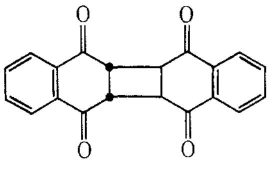
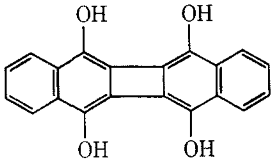
The isolation of the *syn* (I) and *anti* (II) photodimers of 1,4-naphthoquinone was reported recently.[1] In the presence of alkali both I and II led to tetraol (III).[1,2]



I



II

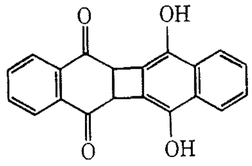


III

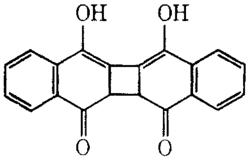
If III is treated with concentrated sulfuric acid, complete ketonization occurs, leading quantitatively to II. Similar treatment of I also produces II. The question as to whether the latter reaction proceeds *via* tetraol III or *via* a partially ketonized derivative thereof urged us to investigate the enolization aptitude of I and II in mild and strong acidic media.

When II was refluxed in acetic acid a yellowish color gradually developed. Concentration of the filtrate, which contained no trace of the monomeric 1,4-naphthoquinone, led to the isolation of orange-red crystals. Molecular weight determination by mass spectrometry[3] (mass 316) and elemental analysis ($C_{20}H_{12}O_4$) indicated that this compound was isomeric with II. The infrared spectrum exhibits a medium peak at 1605 cm$^{-1}$ and a strong peak at 1589 cm$^{-1}$ which may be assigned to two differently environed benzene nuclei, *i.e.*, a naphthalene and a *ortho*-substituted benzene moiety, respectively. A typical olefinic band of medium intensity was observed at 1640 cm$^{-1}$. A sharp carbonylic absorption appears at 1668 cm$^{-1}$. A broad absorption band between 3650 and 3100 cm$^{-1}$, with maximum intensity at 3410 cm$^{-1}$, indicates the presence of hydroxyl groups. The ultraviolet spectrum of this isomeric compound is very similar to that of II, and the *syn* dimer (I).

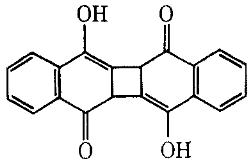
On the basis of the spectroscopic data and chemical properties, the three most likely structures for the isomeric orange-red compound are IV, V, and VI. Structures V and VI, however, are unlikely on account of strain, since the sp$^3$ hybridized carbon atoms in the C$_4$ ring would prevent the adjacent sp$^2$ hybridized carbon atoms from attaining planar configuration, required for significant $\pi$ bonding. This argument is in fact analogous to Bredt's rule.[4] One also has to consider the driving force for the observed enolization of II, which would doubtlessly be aromatization, thus favoring structure IV.



IV

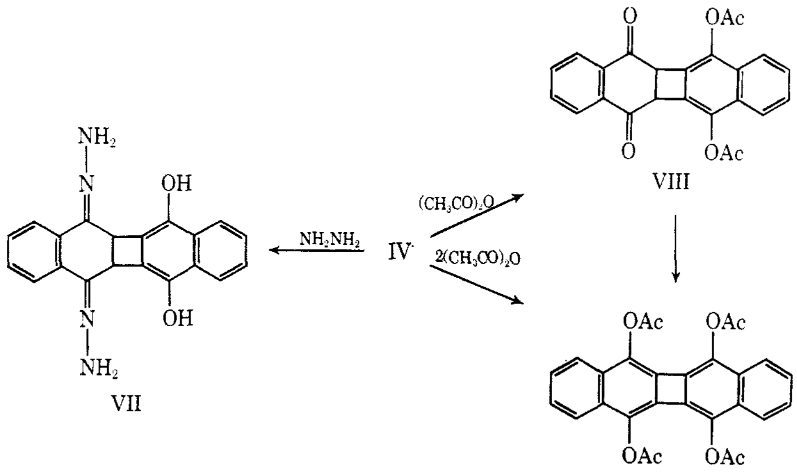


V



VI

The presence of two carbonyl groups in IV was proved by treatment with excess hydrazine, whereby a dihydrazone (VII) was obtained. When IV was refluxed in dioxane containing 2 mol of acetic anhydride the cor-



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