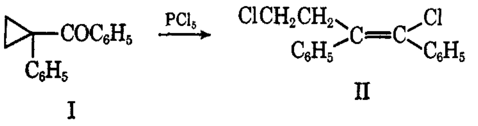
chlorocarbonium ions were not involved were presented. The experimental facts were that different products resulted when certain ketones were brought into contact with phosphorus pentachloride in carbon tetrachloride or in methylene chloride. Acting on information that phosphorus pentachloride was a dimer, P_2Cl_{10}, in carbon tetrachloride and a monomer, PCl_5, in chloroform[4] we accounted for the products isolated by using differences in behavior of P_2Cl_{10} and PCl_5 with the ketones involved. We assumed that PCl_5 was the species present in methylene chloride as this was expected to be more like chloroform than carbon tetrachloride as a solvent.[2,3]

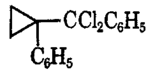
In a recent conversation Professor Shore told me that phosphorus pentachloride is mainly (*ca.* 80%) monomer in *both* CCl_4 and $CHCl_3$ at about 30–35°.[5] Assuming that PCl_5 is mainly monomeric in methylene chloride, new interpretations of the reactions previously discussed[2,3] must be made.

On reaction of phenyl 1-phenylcyclopropyl ketone (I) with phosphorus pentachloride *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) and phenyl(1-phenylcyclopropyl)dichloromethane (III) were formed.[2] In carbon tetrachloride at room temperature only III was obtained (60% of I recovered after 3 days) while at reflux (1.5 hr) 26% II and 70% III were obtained. In methylene chloride II was the main product under all conditions. Furthermore, the rate of reaction in methylene chloride was considerably greater, although not exactly measured.



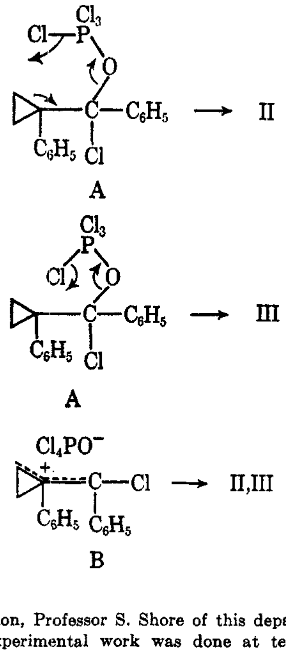
I

II



III

Instead of the explanation previously given[2] the following one, which uses only monomeric PCl_5, is given. In each solvent the complex A, formed by addition of PCl_5 to ketone, is produced. A can further collapse by intramolecular processes to yield II or III as shown. Alternatively A may go to a chlorocarbonium ion (or an ion pair) (B) which yields mainly II. The route *via* the carbonium ion or the ion pair would be favored in methylene chloride as compared to carbon tetrachloride because of the dielectric constant differences (8.7 *vs.* 2.2 D).



Similar explanations can be involved in other cases but will not be discussed in this Note. In conclusion, it is pointed out that arguments previously used to discount the probability of chlorocarbonium ions as reaction intermediates have been revised in the light of new information regarding the species present when phosphorus pentachloride is dissolved in carbon tetrachloride or methylene chloride. The likelihood that chlorocarbonium ions may be reaction intermediates is now favored in certain cases.

Registry No.—PCl_5, 10026-13-8.

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[4] In a conversation, Professor S. Shore of this department gave me this information. The experimental work was done at temperatures below 0° but I was unaware of this fact and assumed that the molecular weights had been determined at room temperature.

[5] These results have recently been obtained in an apparatus which allows for extremely accurate readings of vapor pressure and will be reported by Shore and coworkers.

The Preparation of Nopadiene and 2-Ethylidene-6,6-dimethylbicyclo[3.1.1]-3-heptene

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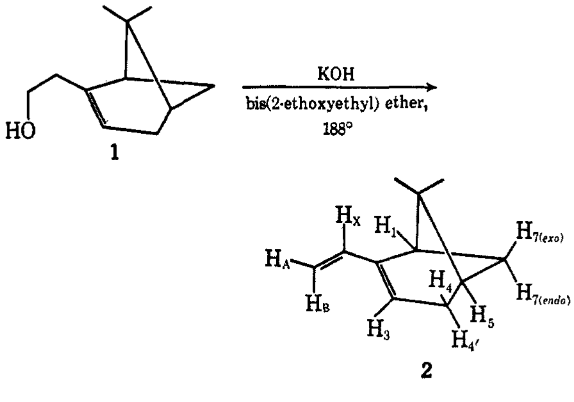
The preparation of nopadiene (**2**) was first reported by Kitchen,[1] who dehydrated the readily available terpene derivative nopol (**1**) using the conditions shown in eq 1. In 1955, Ohloff and Schade[2] reported their results on the dehydration of nopol using a similar procedure (alkali in heterogenous phase at 200°). Under these rather drastic conditions, the latter workers noted that, in addition to nopadiene, there was formed another hydrocarbon to which they tentatively assigned a monocyclic structure possessing three double bonds. In a subsequent publication,[3] however, the base-catalyzed dehydration of nopol was reported to yield,



1

2

(1)

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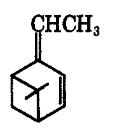
(1) L. J. Kitchen, *J. Amer. Chem. Soc.*, **73**, 2368 (1951).

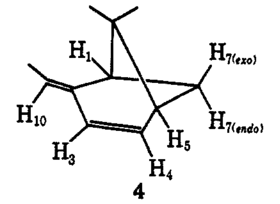
(2) G. Ohloff and G. Schade, *Angew. Chem.*, **67**, 427 (1955).

(3) G. Ohloff, *Chem. Ber.*, **90**, 1554 (1957); *Ann. Chem.*, **627**, 79 (1959).

in addition to nopadiene (**2**), homocymol and an isomeric species which was postulated to be 2-ethylidene-6,6-dimethylbicyclo[3.1.1]-3-heptene (**3**).



3



4

Our interest in nopadiene (**2**) as a precursor to tricyclic pinene derivatives[4] prompted us to reinvestigate the base-catalyzed dehydration of nopol in order to characterize the dehydration products more fully and to explore other methods for obtaining nopadiene (**2**) free from isomeric impurities. In contrast to the base-catalyzed dehydration of nopol which in our hands produces a difficultly separable mixture of olefins in the ratio 65:35,[5] we have found that either pure nopadiene (**2**) or its isomeric species can be prepared by treating the corresponding tosylate of **1** with KO-*t*-Bu–DMSO.[6] Whereas nopadiene is produced exclusively in 65% yield when nopol tosylate is treated with 1.0 equiv of KO-*t*-Bu, the thermodynamically more stable isomeric species is produced (85%) when the elimination is conducted using 3 equiv of base. A detailed nmr analysis of this latter compound (see Experimental Section) serves to establish its structure as **3**. Interestingly, although the isomerization of **2** might be anticipated to produce equal quantities of diastereomers, under our experimental conditions, the ratio of diastereomers is 90:10. On the basis of nmr evidence discussed below we favor **4** as the major product.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR NOPADIENE AT 60 MC

Proton[a]	δ, ppm	Proton	δ, ppm	Coupling constants, Hz	
H_3	5.50	H_X	6.29	J_{AB}	1.0
$H_{7(endo)}$	1.14	$CH_{3(endo)}$	0.80	J_{AX}	10.7
H_A	4.82	$CH_{3(exo)}$	1.32	J_{BX}	17.8
H_B	5.05			J_{gem}	7.70

[a] H_1, H_4, $H_{4'}$, H_5, and $H_{7(exo)}$ are in the region δ 2–2.6 ppm.

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 2-ETHYLIDENE-6,6-DIMETHYLBICYCLO[3.1.1]-3-HEPTANE AT 100 MC

Proton	δ, ppm	Proton	δ, ppm	Coupling constants	Hz	Coupling constants	Hz
H_1	2.93	$H_{7(endo)}$	1.39	$J_{7(exo)-7(endo)}$	8.0	$J_{5-7(exo)}$	5.5
H_3	5.87	H_{10}	5.20	$J_{1-7(exo)}$	5.5	J_{3-5}	1.4
H_4	6.09	$CH_{3(endo)}$	0.71	J_{1-5}	5.5	J_{3-4}	8.5
H_5	2.23	$CH_{3(exo)}$	1.38	J_{1-3}	1.5		
$H_{7(exo)}$	2.43	$CH_{3(vinyl)}$	1.62	$J_{10-CH_3(vinyl)}$	7.0		

Experimental Section[7]

Nopyl tosylate was prepared (90% yield) in the usual manner[8] from nopol (Aldrich) and toluenesulfonyl chloride in pyridine. After recrystallization from pentane, the tosylate had mp 49–50° (lit.[9] mp 49–50). *Anal.* Calcd for $C_{18}H_{24}O_3S$: C, 67.46; H, 7.55. Found: C, 67.30; H, 7.45.

Nopadiene (2) from Nopyl Tosylate.—A mixture of 15.23 g (0.048 mol) of nopyl tosylate, 5.31 g (0.047 mol) of potassium *t*-butoxide, and 100 ml of dimethyl sulfoxide (distilled from CaH_2) was stirred for 22 hr at 75°. The solution was poured into 300 ml of water and the solution was extracted with hexane (three 100-ml portions). The hexane extract was washed with water (five 100-ml portions), dried ($MgSO_4$), concentrated, and distilled giving 4.62 g (65%) of nopadiene (**2**): bp 52.5° (6.0 mm); uv max (hexane), 240 mμ (ε 20,800). *Anal.* Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.90; H, 10.88.

2-Ethylidene-6,6-dimethylbicyclo[3.1.1]-3-heptene (3) from Nopyl Tosylate.—A mixture of 15.0 g (0.047 mol) of nopyl tosylate, 15.0 g (0.134 mole) of potassium *t*-butoxide, and 150 ml of dimethyl sulfoxide (distilled from CaH_2) was stirred for 22 hr at 50°. The solution was added to 300 ml of water and extracted with hexane (three 100-ml portions). The hexane extract was washed with water (five 100-ml portions), dried ($MgSO_4$), concentrated, and distilled giving 5.84 g (84.1%) of **3**: bp 52.5° (6.0 mm); uv max (hexane), 245 mμ (ε 16,000) and 251 mμ (ε 16,000). *Anal.* Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.95; H, 10.74.

Nmr Spectra.—The salient features of the nmr spectrum of nopadiene are summarized in Table I. The three-proton singlets at δ 0.80 and 1.32 are readily assigned to the 6-*endo*- and 6-*exo*-methyls, respectively. Similar assignments have been made for a variety of bicyclic terpenes such as myrtenal,[10,11] α-pinene,[11] and verbenone.[11,12] The rather large difference in chemical shift of these methyls can be ascribed to two effects: (1) the increased shielding of the 6-*endo*-methyl due to its position above the π cloud of the adjacent double bond; or (2) the increased deshielding of the 6-*exo*-methyl due to the anisotropy of the nonplanar cyclobutane ring itself which has been formulated as deshielding axial substituents.[13,14] In the olefinic region, a broad signal at δ 5.50 is assigned to H_3 while the three remaining olefinic protons of the 2-vinyl group give a typical ABX pattern.[15] Assignment of these protons is based on analogy with compounds of similar type[16] and calculated shifts using the substituent

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[4] C. A. Cupas and W. S. Roach, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. 095.

[5] The olefinic mixture was analyzed by gas chromatography using a 150-ft polypropylene glycol capillary column.

[6] D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem. Commun.*, 90 (1968).

(7) Nuclear magnetic resonance spectra were obtained on Varian A-60 and HA-100 spectrometers equipped with spin decouplers. All spectra were run in CCl_4 with chemical shifts reported as δ in parts per million relative to internal tetramethylsilane. Ultraviolet spectra were recorded by a Cary Model 15. Melting points were determined in open glass capillaries and are uncorrected. Analyses are by Galbraith Laboratories, Knoxville, Tenn.

(8) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(9) R. T. Arnold and M. J. Danzig, *J. Amer. Chem. Soc.*, **79**, 892 (1957).

(10) F. Kaplan, C. O. Schulz, D. Weisleder, and C. Klopfenstein, *J. Org. Chem.*, **33**, 1728 (1968).

(11) R. B. Bates and V. P. Thalacker, *ibid.*, **33**, 1730 (1968).

(12) Both ref 10 and 11 contain leading references and detailed summaries of nmr spectral parameters of bicyclo[3.1.1]heptanes and other related bicyclic systems.

(13) N. Nakagawa and S. Saito, *Tetrahedron Lett.*, 1003 (1967); L. R. Subramanian and C. S. Krishna Rao, *ibid.*, 3693 (1967).

(14) For some related examples, see (a) T. W. Gibson and W. F. Erman, *ibid.*, 905 (1967); (b) K. S. Kulkarni, S. K. Parnikar, and S. C. Bhattacharyya, *Tetrahedron*, **22**, 1917 (1966).

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132.

(16) A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965).

constants proposed by Pascual, Meier, and Simon[17] which predict the following trend in chemical shift: $H_A = \delta$ 5.07, $H_B =$ 5.24, $H_X = 6.26$. Finally, a doublet centered at δ 1.14 is assigned to the *endo*-H_7 proton with $J_{gem} = 7.70$ Hz.[18]

A more detailed nmr analysis of **3** was possible using double- and triple-irradiation techniques. The pertinant data are summarized in Table II, p 743.

The singlets at δ 0.71 and 1.38 are assigned to the 6-*endo*- and 6-*exo*-methyls, respectively, while a doublet at δ 1.62 is assigned to the vinylic methyl. A quartet at δ 5.20 is readily assigned to the olefinic proton of the 2-ethylidene grouping, with $J_{vic} = 7.0$ Hz. In analogy with the previously mentioned anisotropy of a rigid nonplanar cyclobutane, the "equatorial" *endo*-H_7 proton appears upfield at δ 1.39 with $J_{gem} = 8.0$ Hz.[19] Triple irradiation of both olefinic protons H_3 and H_4 at δ 5.87 and 6.09 serves to differentiate the remaining protons H_1 and H_5 and *exo*-H_7. In this latter experiment, the triplet of doublets at δ 2.93 collapses to a triplet while the quartet of doublets at δ 2.23 also collapses to a triplet. Since only H_5, and not H_1, would be anticipated to be coupled with both olefinic protons H_3 and H_4 (vicinal and allylic coupling[20]), this latter multiplet is assigned to H_5 while the triplet of doublets at δ 2.93 is assigned to H_1. The overlapping doublet of triplets at 2.43 which was unaffected in this experiment is assigned to *exo*-H_7. Irradiation of the olefinic doublet at δ 5.87 further confirms these assignments and serves to differentiate H_3 and H_4. Here H_1 becomes a triplet while H_5 now collapses to a quartet. Of the olefinic protons H_3 and H_4, only the former would be anticipated to be coupled weakly (allylic coupling[15]) with both bridgehead protons H_1 and H_5. Thus proton H_3 appears at δ 5.87 with the lowest field olefinic resonance at δ 6.09 assigned to H_4. The observed multiplicities of H_1, H_5, and *exo*-H_7, which are essentially first order, are due to a fortuitous equality of three vicinal and a long-range four-bond coupling between the bridgehead protons H_1 and H_5. Similar long-range coupling in bicyclo[3.1.1]heptanes has recently been reported by Kaplan[10] and Bates.[11]

The rather large difference in chemical shift of the bridgehead protons H_1 and H_5 is particularly noteworthy and presumably reflects the greater deshielding experienced by H_1 due to its closer position to the center of the deshielding plane of the adjacent olefinic bond and perhaps a further contribution due to Van der Waals[21] deshielding caused by the adjacent vinyl methyl group.

Registry No.—**2**, 18801-69-9; **3**, 18801-70-2.

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[17] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49** Suppl, 164 (1966).

[18] The absence of vicinal coupling of *endo*-H_7 with the adjacent bridgehead hydrogens in bicyclo[3.3.1]heptane derivatives has previously been noted; see ref 10, 11, and 14a.

[19] The higher field line of this "doublet" falls under the 6-*exo*-methyl resonance. The nmr spectrum of this material shows resonance at δ 1.32 and 1.72 which are attributed to 10% of the diastereomer of **4** which is formed under our conditions. A partially discernable quartet on the high-field side of the δ 5.20 quartet is also indicative of the presence of this species.[17]

[20] S. Sternhell, *Rev. Pure Appl. Chem.*, **14,** 15 (1964).

[21] Our attempts to make a less unambigious stereochemical assignment using the nuclear Overhauser effect[22] were inconclusive.

[22] F. A. L. Anet and A. J. R. Brown, *J. Amer. Chem. Soc.*, **87,** 5250 (1965); J. G. Colson, P. T. Lansbury, and F. D. Saeva, *ibid.*, **89,** 4987 (1967).

The Meerwein Reaction in Amino Acid Synthesis. II. An Investigation of Twenty-one Substituted Anilines[1]

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step 1, diazotization

$$ArNH_3^+Br^- + HNO_2 \rightarrow ArN_2^+Br^- + 2H_2O$$

step 2, Meerwein reaction

$$ArN_2^+Br^- + CH_2{=}CHCOOH \rightarrow ArCH_2CH(Br)COOH + N_2$$

step 3, ammonolysis

$$ArCH_2CH(Br)COOH + 2NH_3 \rightarrow ArCH_2CH(NH_3)^+COO^- + NH_4^+Br^-$$

A major objective of this investigation has been the establishment of the reaction sequence (steps 1–3) as a generalized synthesis of substituted phenylalanines. A part of the objective was obtained with the preparation of the three monochlorophenylalanines.[1b] It was next required that anilines bearing electron-donating groups and anilines bearing electron-withdrawing groups be tested in the reaction sequence in order to establish the generalized synthesis. Twenty-one substituted anilines were submitted to one or several steps of the reaction sequence.[2] Nineteen of these yielded α-bromohydrocinnamic acids (*o*-aminobenzamide failed in the diazotization step; *o*-aminoacetophenone failed in the Meerwein reaction). The nineteen anilines which gave α-bromohydrocinnamic acids showed considerable variation in their behavior in the diazotization and, in particular, Meerwein reactions. These variations, relative to the chloroanilines,[1b] are summarized as follows. (a) Several anilines bearing electron-donating groups did not diazotize smoothly and, in some instances, significant amounts of tars were formed with consequent reduction of Meerwein product in the next step (in this respect *m*-anisidine proved to be particularly poor, with only 90% of the theoretical amount of nitrogen being evolved in the Meerwein reaction); the aryldiazonium bromides formed from anilines carrying electron-donating groups, especially in *ortho* or *para* position, required relatively large amounts of catalyst and high reaction temperatures in order to obtain reasonable reaction rates[3] in the Meerwein reaction. (b) Anilines bearing electron-withdrawing substituents were diazotized with no difficulty. The Meerwein reactions required little catalyst, and in several cases it was found necessary to use only small amounts of copper(I) bromide, low initial temperatures, and an ice bath in order to control the Meerwein reactions. (Thus, the diazotized nitroanilines, under conditions as specified in Table I and described in the Experimental Section, *except* that the catalyst was added to mixtures with initial temperatures of 15°, reacted in an almost explosive manner to give the theoretical amount of nitrogen in *ca.* 3–8 sec, with a temperature rise to 50–60°

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[1] (a) Supported in part by grants from the National Institutes of Health (GM 10560-01, -02) and from Research Corp. Grateful acknowledgement of this support is made here. (b) Part I: G. H. Cleland, *J. Org. Chem.*, **26,** 3362 (1961). The *Chemical Abstracts* treatment of this article [*Chem. Abstr.*, **56,** 12792*i* (1962)] contains critical errors in the example chosen from the experimental Section. Comparison of this part of the original article with the *Chemical Abstracts* review shows that in the latter the amounts of copper(I) bromide catalyst, acrylic acid, and sodium nitrite reported as employed are *twice* those given in the former. The yield of Meerwein product reported as recovered is *also* doubled in the review, giving a value 133% of theory.

[2] Each of the three steps of the reaction sequence was investigated with regard to every aniline tested until conditions were found where reasonable yields were obtained or until failure was acknowledged (one exception: ammonolysis of *m*-acetyl-α-bromohydrocinnamic acid was not attempted). At the same time it should be emphasized that the investigations were exploratory in nature and that in no instance were exhaustive studies made to determine optimum conditions.

[3] A "reasonable rate" is considered here to be one sufficient to give the theoretical amount of nitrogen, or cessation of nitrogen evolution, in 90 min or less. It was necessary to run diazotized *o*-anisidine for 120 min at an average temperature of 44° in order to obtain the theoretical amount of nitrogen.