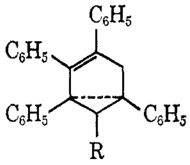
we are forced to conclude that the two cyclopropyl protons of **3** have the same chemical shift, and therefore the coupling between them cannot be observed.[10] There are two effects which probably combine to cause this coincidence. In general, phenyl substituents cause a downfield shift of adjacent protons.[5] For instance, in other studies in this laboratory, it has been found that the cyclopropyl protons of **5** appear at τ 7.6 and of **6** at τ 6.2.[5] The absence of the C-5 phenyl in **3** must cause an upfield shift of the C-6 proton from its chemical shift in **6**. In **3**, the C-4 and C-6 phenyls must be causing a downfield shift of the C-5 proton.



5, R = H
6, R = C_6H_5

The nmr spectrum of the diol supports our structural assignment. There is a two-proton AB pattern at τ 5.68 and 6.27 (J = 7.5 cps) attributable to the benzylic proton and proton adjacent to the hydroxyl group, a two-proton AB pattern at τ 7.29 and 7.47 (J = 4.0 cps) for the cyclopropyl protons, and a two-proton broad multiplet which is not observed after 1 drop of deuterium oxide was added to the sample tube and is therefore attributed to the hydroxyl protons. The 4.0-cps coupling constant of the cyclopropyl protons is evidence that they are *trans*.[11] The spectra of both **3** and **4** show that the benzylic proton (on C-4) and the bridgehead proton (on C-5) are not coupled. If they are *trans*, molecular models show that the dihedral angle is about 110°; if they are *cis*, it is about 0°. On the basis of the Karplus relation the dihedral angle must be 90° if the coupling constant is zero.[12] In support of this conclusion is the observation of Bergvist and Norin that the coupling constant of the C-4 and C-5 protons of (−)-thujone is zero.[13] Thus, we conclude that the protons must be *trans* and the complete stereochemistry of **3** and **4** is as shown.

In summary, we have shown that irradiation of **1** yields **3**, rather than **2** as was previously proposed.[3] There is insufficient evidence to permit determination of the immediate precursor of **3**. Although it has been assumed that trienes are the precursors of bicyclo[3.1.0]hexenes, this has not been rigorously proven.[4b,14] Presumably the conversion of trienes to dienes and the isomerization of trienes is reversible.[4,5] Careful study may show that the corresponding 2,3,5,6-tetraphenylcyclohexadiene and at least one isomeric triene is present in the photomixture of **1**.

Experimental Section

Melting points were determined in an oil bath and are uncorrected. Infrared spectra were determined in carbon tetrachloride using a Perkin-Elmer Infracord Model 137. Ultraviolet spectra were taken in acetonitrile on a Perkin-Elmer Model 202 spectrometer. Nmr spectra were recorded on Varian A-60 (60 MHz) and HA-100 (100 MHz) instruments. Mass spectra were determined on a Varian Model M-66 instrument.

1,2,4,6-Tetraphenylbicyclo[3.1.0]cyclohexene (3).—The procedures of Dessy were followed,[3] except that triene **1** was irradiated with a Hanovia high-pressure mercury lamp in an immersion apparatus fitted with a Pyrex filter. The material so prepared possessed all the published properties[3] except details of the nmr spectrum which follow: τ 2.4–3.4 (20 H, multiplet, phenyl H), 4.3 (1 H, broad singlet, vinyl H), 5.9 (1 H, doublet, J = 2.0 cps, allylic H), 7.7 (2 H, singlet which also has unresolved fine structure on both shoulders, cyclopropyl H). A double irradiation was performed: irradiation at τ 4.3 collapsed the doublet at 5.9 to a singlet; irradiation at τ 5.9 narrowed the broad singlet at 4.3; irradiation at τ 7.7 collapsed the broad singlet at 4.3 to a doublet (J = 2.0 cps). The high-field singlet was not noticeably affected by these experiments.

Degradation of 3 by Osmium Tetroxide.—To a 250-ml, round-bottomed flask was added 108 mg (0.281 mmole) of **3**, 10 ml of pyridine, 100 ml of dry ether, and 150 mg (0.59 mmole) of osmium tetroxide. The flask was stoppered, wrapped in aluminum foil, and allowed to stand at room temperature for 1 week.

The solvent was removed and the brown oil was placed in a vacuum oven for 1 hr to remove the last traces of pyridine. The oil was taken up in ether and cooled in an ice bath, and 550 mg (0.68 mmole) of lithium aluminum hydride was added. The slurry was stirred for 1 hr at room temperature and cooled in an ice bath, and the salts were precipitated with saturated ammonium chloride solution. The organic layer was decanted and the salts were washed once with water. The combined ethereal layers were dried over magnesium sulfate and the solvent was removed to yield 61 mg of a brown oil. An attempted crystallization gave impure brown crystals.

The crystals and mother liquors were recombined and filtered through a silica gel column (6 × 0.8 cm). Two fractions were taken: the first, eluted with 10 ml of benzene, contained 3 mg of a colorless oil; the second, eluted with 15 ml of ether, contained 59 mg of a white solid shown to be **4** (50% over-all yield of diol). Two crystallizations from benzene–methylcyclohexane of the second fraction gave the analytical sample: mp 184.8–185.8°; infrared, ν_{max} 3540 cm^{-1}; ultraviolet, λ_{max} 259 mμ (ϵ 880) and λ_{sh} 220 mμ (ϵ 29,000); nmr, τ 2.4–7.4 (20 H, multiplet, phenyl H), 5.68 (1 H, doublet, J = 7.5 cps, C-3 or benzylic H), 6.28 (1 H, doublet, J = 7.5 cps, benzylic or C-3 H), 7.29 (1 H, doublet, J = 4.0 cps, cyclopropyl H), 7.47 (1 H, doublet, J = 4.0 cps, cyclopropyl H), and 7.7–8.1 (2 H, multiplet, hydroxyl H; the signal of these protons disappears when 1 drop of deuterium oxide is added to the sample); mass spectrum, M = 418, 400, and 384 (base peak).

Anal. Calcd for $C_{30}H_{26}O_2$ (418.54): C, 86.09; H, 6.26. Found: C, 85.96; H, 6.22.

Registry No.—1, 13573-38-1; 3, 13573-39-2; 4, 13573-40-5.

---

[10] Reference 7, p 89.

[11] W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).

[12] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 49–53.

[13] M. S. Bergvist and T. Norin, *Arkiv Kemi*, **22**, 137 (1964).

[14] See E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *Tetrahedron Letters*, 935 (1967). Generalization of their conclusion to polyolefins awaits determination of the multiplicity of the states involved in the various reactions, especially since their bicyclo[3.1.0]hexene can be viewed as arising from a normal photochemical dienone rearrangement [see H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966), and references therein].

Ketimine Syntheses. Use of Titanium Tetrachloride in a New Procedure for Their Preparation

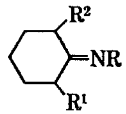
HAROLD WEINGARTEN, JOHN P. CHUPP, AND WILLIAM A. WHITE

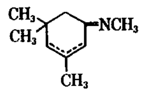
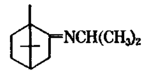
Monsanto Company,
Central Research Department and Agricultural Division,
Research Department, St. Louis, Missouri 63166

Received January 11, 1967

Various preparative procedures for certain ketimines from a variety of cyclohexanones and primary amines were evaluated from the standpoint of yield and con-

TABLE I
PREPARATION OF KETIMINES



Structure			Registry no.	Method[a]	Yield,[b] %	C=N/ C=O[c]	Bp (mm), °C	$n^{24}\text{D}$	Empirical formula	Calcd, %			Found, %		
R	R¹	R²								C	H	N	C	H	N
CH_3	H	H	6407-35-8	A	80		70–74 (35)	1.4772[d]	$C_7H_{13}N$						
$(CH_3)_2CH$	H	H	13652-31-8	A	80		70–74 (28)	1.4615	$C_9H_{17}N$	77.63	12.31	10.06	77.46	12.75	9.92
CH_3	CH_3	H	13484-03-2	A	<20[e]		72–74 (25)								
H	CH_3	CH_3	13652-33-0	B	55[e]	0.78	61–65 (10)		$C_8H_{15}N$						
CH_3	CH_3	CH_3	13652-34-1	B	*e*	0.71	61–70 (10)		$C_9H_{17}N$						
C_2H_5	CH_3	CH_3	13652-35-2	B	<10[e]	0.26	61–70 (10)		$C_{10}H_{19}N$						
H	$(CH_3)_3C$	*cis*-CH_3	13652-36-3	B	50	0.48	93–94 (12)	1.4694	$C_{11}H_{21}N$	78.97	12.65	8.37	78.94	12.85	8.19
		trans-CH_3	13652-56-7												
$CH_2{=}CHCH_2$	CH_3	H	13652-37-4	C	74		76–78 (10)	1.4796	$C_{10}H_{17}N$	79.41	11.33	9.26	79.01	11.60	9.15
$(CH_3)_2CH$	CH_3	H	13652-38-5	C	30	1.42	59–60 (8)	1.4564	$C_{10}H_{19}N$			9.14			8.92
$CH_2{=}CHCH_2$	C_2H_5	H	13652-39-6	C	66	2.6	88–91 (10)	1.4795	$C_{11}H_{19}N$	79.94	11.59	8.48	79.85	11.69	8.18
$CH_2{=}CHCH_2$	CH_3	CH_3	13652-40-9	C	<30[e]	0.27	75 (10)								
$CH_3OCH_2CH_2$	H	H	13652-41-0	D	60		72–75 (3)	1.4741	$C_9H_{17}NO$	69.63	11.04	9.02	68.73	10.90	9.14
$CH_3OCH_2CH_2$	CH_3	H	13652-42-1	D	79	3.6	98–100 (15)	1.4672	$C_{10}H_{19}NO$	70.96	11.31	8.28	70.84	11.52	8.24
$CH_3OCH_2CH_2$	C_2H_5	H	13652-43-2	D	69		113 (13)	1.4684	$C_{11}H_{21}NO$	72.08	11.55	7.64	72.30	11.84	7.69
$CH_3OCH_2CH_2$	$(CH_3)_2CH$	H	13652-44-3	D	79	6.0	112–114 (10)	1.4690	$C_{12}H_{23}NO$	73.04	11.75	7.10	72.40	11.73	7.16
$CH_3OCH_2CH_2$	CH_3	CH_3	13652-45-4	D	47	2.6	95–96 (10)	1.4666	$C_{11}H_{21}NO$	72.08	11.55	7.64	71.40	11.47	7.69
C_2H_5	CH_3	H[f]	13652-46-5	E	53	5.4	81 (14)	1.4642	$C_{10}H_{20}N$	77.85	13.07	9.08	78.39	12.54	8.67
C_2H_5	$(CH_3)_3C$	H	13562-47-6	E	56	4.5	94–97 (12)	1.4665	$C_{12}H_{23}N$	79.49	12.76	7.73	79.71	12.79	7.41
$(CH_3)_2CH$	CH_3	CH_3	13652-48-7	E[g]	79	13.5	65–71 (10)	1.4554	$C_{11}H_{21}N$	78.97	12.65	8.37	78.90	13.00	7.96
$CH_3OCH_2CH_2$	$(CH_3)_3C$	H	13652-49-8	E[h]	61	3.0	59–61 (1)	1.4680	$C_{13}H_{25}NO$	73.88	11.92	6.63	74.61	12.07	6.41
CH_3	$(CH_3)_3C$	*cis*-CH_3	13652-50-1	E[g]	10	1.0	95 (15)	1.4702	$C_{12}H_{23}N$	79.49	12.76	7.73	79.22	12.82	7.84
		trans-CH_3	13717-35-6												
$CH_2{=}CHCH_2$	$(CH_3)_2CH$	$(CH_3)_2CH$	13652-51-2	E	70	3.8	133–134 (14)	1.4763	$C_{15}H_{27}N$	81.38	12.29	6.32	81.02	12.19	6.69
		2,3-	13652-52-3	E	28		92 (15)	1.4935	$C_{10}H_{17}N$	79.41	11.33	9.26	79.50	11.23	9.31
		3,4-	13652-57-8												
			13652-53-4	E[i]	67		98 (17)	1.4690	$C_{13}H_{23}N$	80.76	11.99	7.25	80.63	12.00	7.30

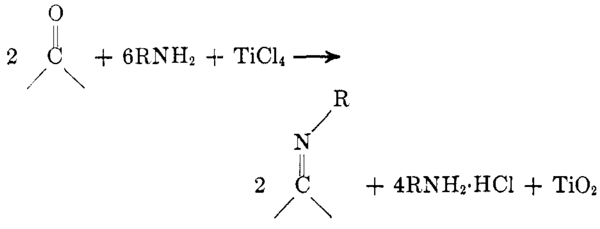
[a] See text and Experimental Section for details on methods and spectral data. [b] Unless otherwise indicated, yield represents conversion to pure distilled imine, based on ketone charged. [c] Absorption intensities measured by infrared at *ca.* 5.9–6.2 and 5.8–6.1 μ, respectively. Although differing in magnitude, the molar absorption intensities of the cyclohexanones at these wavelengths are approximately two times those of imines. [d] Reference 1 gives $n^{20}\text{D}$ 1.4747. [e] Product contained appreciable ketone on distillation and no attempt was made to obtain pure imine. Yield estimated from infrared, nmr, or vpc. [f] Starting ketone is 2,3-dimethylcyclohexanone. [g] Method B gave no imine. [h] Method D gave no imine. [i] Method A gave no imine.

venience. A number of imines were thus prepared by dehydration with potassium hydroxide (method A),[1] heat treatment under pressure (B), and water azeotrope in low-boiling (C) or high-boiling solvent (D).

The above-listed methods, each useful and convenient enough within their respective limitations, were not sufficient to prepare ketimines in the following two categories: (1) ketimines arising from volatile or moderately volatile amines and moderately to highly substituted ketones, where method D cannot be employed owing to the low boiling point of the amine, and (2) ketimines from highly hindered ketones or amines where even the higher temperatures encountered with method D are insufficient to give good yield.

In the course of investigating the synthetic applications of titanium tetrachloride (registry no. 7550-45-0) and titanium amides, we found these reagents quite satisfactory in effecting conversion of secondary amines and ketones to enamines.[2] Our interest in extending the synthetic applications of these reagents, coupled with the knowledge gained through previous studies of deficiencies in other methods of ketimine preparation, prompted us to investigate the utility of relatively cheap and available titanium tetrachloride. The results are complied in the Table I. Generally, the ketimines are listed in order of increasing substitution, hence the indicated change in the mild conditions of method A to the more severe conditions of C and D. With few exceptions, it can be assumed that a ketimine listed in the table cannot readily be made by a method listed above it. Finally, the ketimines prepared with titanium tetrachloride (method E) are listed at the bottom of the table.

The amounts of reactants employed in method E were largely determined by eq 1. Slight excesses over



$$2\ \mathrm{{>}C{=}O} + 6\mathrm{RNH_2} + \mathrm{TiCl_4} \longrightarrow 2\ \mathrm{{>}C{=}N{-}R} + 4\mathrm{RNH_2{\cdot}HCl} + \mathrm{TiO_2} \qquad (1)$$

stoichiometry of both amine and titanium tetrachloride seemed to give best results, although we did not make extensive studies of reactant ratios to optimize yields.

Mechanistically, we regard the reaction to be exactly analogous to the enamine synthesis previously reported.[2] Briefly, the two main features are coordination of the carbonyl oxygen with the titanium atom, thereby preparing the carbonyl group for reaction with amines, and the transfer of the carbonyl oxygen atom from carbon to titanium.

We have included certain pertinent infrared and nmr spectral data in the Experimental Section. These physical measurements, plus the elemental analyses, confirm the imine structures assigned. This becomes important with materials like the camphorimine, where structures arising from acid-catalyzed rearrangement are possible alternatives, or with N-methylisophoroneimine, where the nmr spectrum confirms the presence of two imines, differing only in the position of the *endo* double bond. Also, imines from 2-*t*-butyl-6-methylcyclohexanone appear to be mixtures arising from *cis* and *trans* substitution of the alkyl groups attached to the cyclohexanone ring. Finally, identical alkyl groups in the 2,6 position of the cyclohexylidene moiety appear to show magnetic nonequivalence, probably owing to one being *syn* and the other *anti* to the =N-alkyl group.

Experimental Section

The nmr spectra were recorded on a Varian Model A-60 with chemical shifts given in parts per million from tetramethylsilane as internal standard, while the infrared spectra were recorded on a Beckman infrared Va. All elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. The following detailed procedures will serve to illustrate the various methods discussed and describe representative preparations of the imines listed in Table I.

Method A.—This method, already described,[1] gave optimum yields when excess amine over ketone was employed. KOH (85%) was the best dehydrating agent found.[3]

Method B. 2-*t*-Butyl-6-methylcyclohexylideneamine.—2-*t*-Butyl-6-methylcyclohexanone (362.5 g, 21.6 moles) was added to a 1.4-l. autoclave with 50 g of KOH pellets. After 300 g of anhydrous ammonia was charged, the autoclave was heated to 260°, whereby 6400 psi developed. The material was heated *ca.* 60 hr, then cooled to give C=O/C=N infrared absorption intensity (5.9 and 6.05 μ, respectively) of 1.0/0.36. The mixture was placed in 500 ml of ether and treated with excess anhydrous hydrogen chloride to give 150 g of iminohydrochloride salt (170 g of ketone recovered). The imino salt (75 g) was treated with sodium carbonate solution, extracted with ether, and dried over magnesium sulfate. Vacuum removal of the ether gave 47.2 g of imine, which distilled at 93–94° (12 mm). The infrared spectrum showed a maximum at 6.1 μ (C=N) and the nmr spectrum (CCl_4) displayed a 6-methyl doublet (J = 7 cps) at τ 0.92 and 2-*t*-butyl at 0.95 and 1.05. The ratios of these two latter absorptions varied with each preparation. We conclude that this reflects varying amounts of *cis*- and *trans*-2-*t*-butyl-6-methylcyclohexylidene content.

Method C. N-Allyl-2-ethylcyclohexylideneamine.—2-Ethylcyclohexanone (37 g, 0.3 mole) was mixed with 50 ml of allylamine in 200 ml of pentane and water was removed by azeotrope over a period of several hours. At the end of this time, the C=O/C=N absorption intensity at *ca.* 6 μ was 0.14/0.36. Distillation of the imine at 88–91° (10 mm) gave 32.9 g. In a like manner, N-isopropyl-2-methylcyclohexylideneamine was prepared from 2-methylcyclohexanone and isopropylamine using 2-methylbutane in place of pentane.

Method D. N-(2-Methoxyethyl)-N-2,6-dimethylcyclohexylideneamine.—2-Methoxyethylamine was mixed in 200 ml of benzene with 2,6-dimethylcyclohexanone (31 g, 0.25 mole). After the 1 hr of reflux, 2 drops of methylsulfonic acid were added and the material was continually refluxed for 4 days, after which time the C=O/C=N absorption intensity at *ca.* 6 μ was 0.09/0.23. The material was distilled through a 2-ft clay saddle packed column to give 21.6 g of pure imine at 95–96° (8–11 mm). The infrared spectrum showed a maximum at 6.02 μ (C=N) and the nmr (pure liquid) showed two methyl doublets (J = 7 cps) of equal intensity. This could be due to an equal mixture of *cis*- and *trans*-2,6-dimethylcyclohexylideneimine, but it more likely represents *syn*- and *anti*-methyl groups within the same imine.

Method E.—The use of the titanium tetrachloride method is illustrated by the representative procedures 1–4.

1. **N-Isopropyl-N-(2,6-dimethylcyclohexylidene)amine.**—2,6-Dimethylcyclohexanone (63 g, 0.5 mole) was dissolved in 300 ml of ether with 1.5 moles (88.5 g) of isopropylamine. To this solution was added a pentane solution (200 ml) containing 48 g (0.25 mole) of $TiCl_4$. (*Caution:* $TiCl_4$ reacts exothermically with ether.) The addition was made over a period of *ca.* 45 min. After permitting the stirred solution to come to room temperature over 1 hr more, the mixture was refluxed for 1.5 hr and then permitted to stand at room temperature overnight. The final absorption ratio C=O/C=N after this time was 0.025/33.0. The ether solution was filtered, salt cake washed with more

---

[1] R. N. Blomberg and W. F. Bruce, U. S. Patents 2,700,681 and 2,700,682 (1955).

[2] H. Weingarten and W. A. White, *J. Org. Chem.*, **32**, 213 (1967).

[3] K. N. Campbell, A. H. Sommer, and B. K. Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944).

ether, the solvent removed, and the residue distilled. Less than 1 g of forerun was collected, while imine (65.5 g) distilled at 69–71° (10 mm). The infrared spectrum showed a maximum at 6.09 μ (C=N) and the nmr spectrum (pure liquid) showed two overlapping methyl doublets of *ca.* equal magnitude (J = 7 cps) at τ 0.96 and 1.02 assigned to the ring methyl groups, and a methyl doublet (J = 7 cps) at 1.06 (6 H) for the isopropyl group. It is unclear whether these multiplets, as in example D, reflect *cis–trans* isomerism or *syn* and *anti* ring methyl groups within the same compound.

2. **N-Methyl-N-(2-*t*-butyl-6-methylcyclohexylidene)amine.**—2-*t*-Butyl-6-methylcyclohexanone (101.0 g, 0.6 mole) was placed in a 2-l. flask and mixed with a solution of ether (450 g) containing 59 g of condensed anhydrous methylamine at −10°. A solution of 36 ml of $TiCl_4$ (62 g, 0.326 mole) contained in 200 ml of pentane was added over 45 min. After all of the $TiCl_4$ was added, the material was allowed to warm to room temperature over 1 hr, then heated to reflux (35–40°) for 0.5 hr. After this time, a sampling showed only C=O (no C=N). The bright orange-red reaction mixture was stripped of the low-boiling ether–pentane solvent and *ca.* 500 ml of toluene added. The material was then heated to 110°. After 5 hr, the material was cooled and allowed to stand overnight. The brown-tan mixture was sampled at this time and found to have a ratio C=O/C=N of 1/1. An additional 5 hr heating did not change this ratio. The material was cooled and filtered and the salt cake washed with more toluene. The filtrate and washings were combined, the solvent was removed, and the residue was filtered through clay. The oil was taken up in ether and treated with anhydrous HCl to give a syrupy salt. The ether was decanted, the syrup dissolved in cold water, shaken with ether twice, and the resulting aqueous solution treated with Na_2CO_3 and ether. The ether layer was dried over $MgSO_4$, evaporated, and the residue distilled to give 11 g of pure imine at 95° (15 mm). The infrared spectrum showed the maximum at 6.06 μ (C=N) and the nmr displayed two imine *t*-butyl groups at *ca.* τ 0.9 and 0.97 of unequal intensities and two methyl peaks of different magnitude at *ca.* 2.98 and 3.04 (each split by long-range coupling into doublets, J = 1 cps). We interpret this spectra as arising from a mixture of *cis-* and *trans*-2-*t*-butyl-6-methylcyclohexylidenimine.

3. **N-Methylimine of Isophorone.**—Isophorone (83 g, 0.6 mole) was placed in a 2-l. flask with 1.9 moles (59 g) of anhydrous methylamine dissolved in 400 ml of toluene at −10°. Then 36 ml of $TiCl_4$ (0.326 mole) dissolved in *ca.* 50 ml of toluene was added. The material turned dark brown. After permitting the reaction mixture to warm to room temperature, an aliquot showed the presence of some C=O. The material was heated at 90° for 2 hr, cooled, allowed to stand overnight, filtered, and the salt cake washed with more toluene. After removing solvent from the combined filtrate and wash, the residue was distilled through a Vigreux column to give only one fraction at 92° (15–16 mm) (25.7 g). The distillate, although originally colorless, turned a dark blood-red on even minimum exposure to air. The decreased yield is at least partially due to polymerization, as a large residue was left after distillation. The infrared spectrum showed maxima at 6.15 (C=N) and 6.22 μ (C=C) and the nmr showed two singlets of slightly different magnitude for the *gem*-dimethyl group at *ca.* τ 0.78 and 0.84, a broad resonance at 2.96 for NCH_3, and two multiplets in 55:45 intensity ratio for one olefinic proton at 5.74 and 6.8, respectively. We interpret these results to reflect the presence of a nearly equal mixture of two imines differing only in a 2,3- and 3,4-*endo* double bond.

4. **N-Isopropylcamphorimine.**—*dl*-Camphor (30.4 g, 0.2 mole) was mixed with 0.7 mole of isopropylamine (41.3 g) in toluene and to this solution at 0–5° was added 13.5 ml of $TiCl_4$ (22.7 g) dissolved in toluene. After addition, 1 aliquot was taken which, however, on mixing with pentane gave a solid and little residue on evaporation of the filtered pentane–toluene solution. This small residue contained only C=N, however. The reaction mixture was then heated *ca.* 7 hr at reflux with slow precipitation from hot toluene of amine hydrochloride. After standing over the weekend at room temperature, the material was filtered through clay twice *after* adding 500–700 ml of pentane. The toluene–pentane solution was vacuum treated to remove solvent and the residue distilled through an 18-in. Vigreux column to give 26.0 g, bp 98° (17 mm). No forecut except toluene and only a trace of residue was encountered. The infrared spectrum showed one maximum at 5.91 μ (C=N) and the nmr showed spectra with a similar absorption pattern from ring methyl groups as found in camphor (three singlets in the τ 0.9–1.2 region) plus a doublet for the N-isopropyl group partially superimposed upon this pattern.

Acknowledgment.—We gratefuly acknowledge Dr. J. F. Olin for his generous supplies of certain substituted ketones employed in this study.

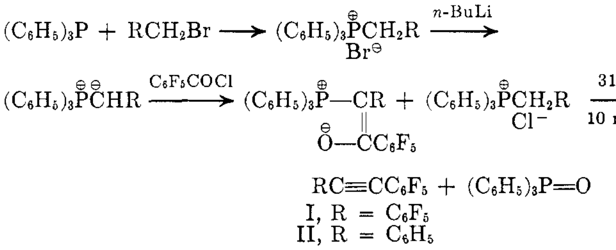
Bis(pentafluorophenyl)acetylene and 2,3,4,5,6-Pentafluorodiphenylacetylene

Robert Filler and Edward W. Heffern

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

Received April 20, 1967

We wish to report the synthesis and properties of bis(pentafluorophenyl)acetylene (I) and 2,3,4,5,6-pentafluorodiphenylacetylene (II). The preparation of these new compounds was accomplished using a modification of the method of Trippett and Gough,[1] as shown in eq 1.



$$(C_6H_5)_3P + RCH_2Br \longrightarrow (C_6H_5)_3\overset{\oplus}{P}CH_2R\ \underset{}{Br^{\ominus}} \xrightarrow{n\text{-BuLi}}$$

$$(C_6H_5)_3\overset{\oplus}{P}\overset{\ominus}{C}HR \xrightarrow{C_6F_5COCl} (C_6H_5)_3\overset{\oplus}{P}-\underset{\overset{\ominus}{O}-\underset{}{C}C_6F_5}{\underset{\|}{C}}R + (C_6H_5)_3\overset{\oplus}{P}CH_2R\ Cl^- \xrightarrow[10\ mm]{310°}$$

$$RC{\equiv}CC_6F_5 + (C_6H_5)_3P{=}O \quad (1)$$

I, R = C_6F_5
II, R = C_6H_5

The phosphonium bromides, obtained in 95–97% yield, were converted into the ylides, which were not isolated but allowed to react directly with pentafluorobenzoyl chloride to give the corresponding acylarylidenetriphenylphosphorane (86% when R = C_6H_5, 74% when R = C_6F_5, based on acid chloride). Pyrolysis of the phosphoranes produced the acetylenes, each in 95% yield. The over-all yields of I and II were 68 and 77%, respectively.

The unsymmetrical acetylene, II, was also prepared in one step, in 20% yield, by reaction of iodopentafluorobenzene with cuprous phenylacetylide in dimethylformamide solution[2] (eq 2).

$$C_6F_5I + CuC{\equiv}CC_6H_5 \xrightarrow{DMF} C_6F_5C{\equiv}CC_6H_5 + CuI \quad (2)$$

The infrared and nmr spectra of these compounds were consistent with the acetylenic structures. Compound II exhibited weak absorption at 2240 cm^{-1} (C≡C stretch), whereas I, as expected from its symmetrical structure, did not possess this band. The ultraviolet spectra of I and II in isooctane were very similar to that of diphenylacetylene (Table I).

In contrast to diphenylacetylene, both I and II failed to absorb bromine in carbon tetrachloride solution. This behavior reflects the significant electron-withdrawing effect of the pentafluorophenyl groups in reducing the nucleophilic character of the triple bond. Both I and II were excellent dienophiles and reacted

---

[1] S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962).

[2] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966).