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.

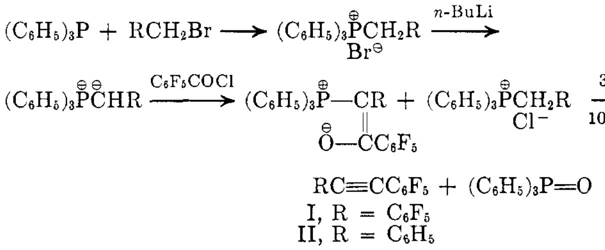
Bis(pentafluorophenyl)acetylene and 2,3,4,5,6-Pentafluorodiphenylacetylene

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.



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

$$(C_6H_5)_3\overset{\oplus}{P}\overset{\ominus}{C}HR \xrightarrow{C_6F_5COCl} (C_6H_5)_3\overset{\oplus}{P}\text{—}\underset{\overset{\ominus}{O}\text{—}CC_6F_5}{\underset{\|}{CR}} + (C_6H_5)_3\overset{\oplus}{P}CH_2R\ Cl^- \xrightarrow[10\text{ mm}]{310^\circ}$$

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

$$\text{I, } R = C_6F_5 \qquad \text{II, } R = C_6H_5$$

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} ($C{\equiv}C$ 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).

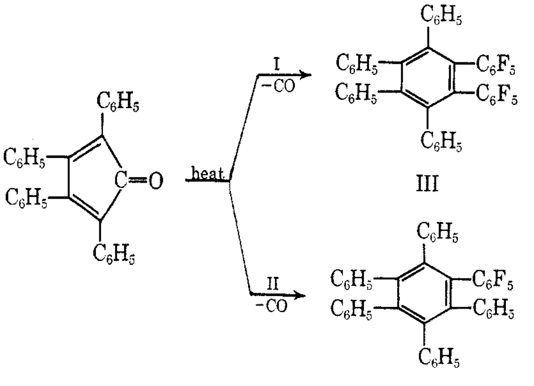
TABLE I

ULTRAVIOLET SPECTRA OF DIPHENYLACETYLENES

$C_6H_5C{\equiv}CC_6H_5$		$C_6F_5C{\equiv}CC_6F_5$ (I)		$C_6F_5C{\equiv}CC_6H_5$ (II)	
λ, mμ (ϵ^a)		λ, mμ (ϵ^a)		λ, mμ (ϵ^a)	
297	29,400	295	26,900	297	29,800
288	23,250	284	20,000 sh	287	23,500 sh
279	33,000	277	33,600	280	33,400
272	25,200	268	23,000 sh	271	23,000 sh
264	23,450	263	23,100	265	22,100
				253	12,500 sh

[a] M^{-1} cm^{-1}.

readily with tetraphenylcyclopentadienone to give the hexaarylbenzenes III and IV, respectively, each in 60% yield (eq 3).



(3)

The proton magnetic resonance (pmr) spectrum of III revealed two resonances in the phenyl region with integrated areas of 1:1. Compound IV also showed two resonances, but with an area ratio of 3:2.

Further studies of polyfluoroaryl acetylenes are in progress.

Experimental Section

Preparation of Benzyltriphenylphosphonium Bromide.—A solution of triphenylphosphine (21 g, 0.08 mole) and α-bromotoluene (27 g, 0.16 mole) in anhydrous benzene (300 ml) was heated under reflux for 5 hr. The resulting white precipitate was filtered, washed with two 50-ml portions of hot benzene, and dried in a vacuum desiccator charged with phosphorus pentaoxide, to give 33 g (95.5% based on the triphenylphosphine) of product. Recrystallization of the phosphonium salt from a 1:1 mixture of 95% ethanol–ethyl acetate produced white crystals, mp 296–298°.

Preparation of 2,3,4,5,6-Pentafluorobenzyl Bromide.—A procedure similar to that described by Birchall and Haszeldine[3] was used. Bromine (30 g, 0.188 mole) was added dropwise to 2,3,4,5,6-pentafluorotoluene (30 g, 0.0164 mole) over a period of 1.5 hr. During the addition and subsequent reaction, the mixture was kept under reflux and irradiated with a 150-w bulb. Heating and irradiation were continued for an additional 45 min and the mixture was then cooled, dissolved in ether (70 ml), and washed with 1% aqueous sodium hydroxide solution (100 ml), 2% sodium sulfite solution (100 ml), and water. The dried (sodium sulfate) ethereal layer was distilled to give 34 g (79%) of 2,3,4,5,6-pentafluorobenzyl bromide, bp 173–176°.

Preparation of 2,3,4,5,6-Pentafluorobenzyltriphenylphosphonium Bromide.—A solution of triphenylphosphine (37 g, 0.14 mole) and 2,3,4,5,6-pentafluorobenzyl bromide (18.5 g, 0.07 mole) in 200 ml of anhydrous benzene was heated under reflux for 5 hr. The white precipitate which formed was filtered, washed with two 75-ml portions of hot benzene, and dried in a vacuum desiccator to give 35.7 g (97.5%, based on the 2,3,4,5,6-pentafluorobenzyl bromide) of product. Recrystallization from a 1:1 mixture of 95% ethanol–ethyl acetate produced white crystals, mp 247–249°.

Preparation of Pentafluorobenzoyl Chloride.—A procedure similar to that described by Tamborski[4] was used. Pentafluorobenzene (34 g, 0.2 mole) in 70 ml of anhydrous diethyl ether was added dropwise to a cooled (−70°), stirred solution of *n*-butyllithium (0.2 mole) in hexane solution over a period of 1 hr. The reaction was conducted under an atmosphere of nitrogen and the temperature was not allowed to rise over −55° during the addition. After stirring for 2 hr, the solution was carbonated by bubbling dry carbon dioxide into the reaction vessel for 2 hr at −70°. The mixture was allowed to warm to room temperature with continued carbonation. The reaction mixture was then hydrolyzed with a large volume of 6 *N* hydrochloric acid (400 ml) and extracted with ether. The dried ether extract was placed on a rotatory evaporator to remove the ether. Crude pentafluorobenzoic acid (40 g, 95%) remained. The acid was then added to an excess of thionyl chloride and the mixture heated under reflux for 24 hr. Distillation gave 42 g (90%, based on pentafluorobenzene) of pentafluorobenzoyl chloride, bp 158–159°.

Preparation of α-2,3,4,5,6-Pentafluorobenzoylbenzylidenetriphenylphosphorane.—Benzyltriphenylphosphonium bromide (15 g, 0.035 mole) was added in portions to a solution of *n*-butyllithium (0.035 mole, 23 ml of 1.6 *M* solution in hexane) in anhydrous benzene (200 ml) over a period of 0.5 hr. During the addition and the subsequent reaction, a nitrogen atmosphere was maintained. The reaction temperature was maintained at approximately 15°. Stirring was continued for 2 hr after addition of the phosphonium salt had been completed.

To the resultant orange solution was added 2,3,4,5,6-pentafluorobenzoyl chloride in benzene (3.2 g in 50 ml of benzene, 0.014 mole) dropwise over a period of 1.5 hr. After 15 min of additional stirring, the mixture was filtered and the solid residue was washed twice with hot benzene. Recrystallization of the residue from ethanol–ethyl acetate gave 5.7 g of the phosphonium chloride salt (90%, based on acid chloride). The benzene from the filtrate was stripped off, leaving a yellowish orange solid (8.5 g). Recrystallization of the solid from ethanol–water gave white crystals, mp 245–247°. Recrystallization of the solid from ethyl acetate gave yellow crystals, mp 244–247°. The yield of the α-2,3,4,5,6-pentafluorobenzoylbenzylidenetriphenylphosphorane was 6.2 g (86%, based on acid chloride).

Preparation of α,2,3,4,5,6-Pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane.—2,3,4,5,6-Pentafluorobenzyltriphenylphosphonium bromide (15 g, 0.0287 mole) was added in portions to a solution of *n*-butyllithium (0.0287 mole, 18 ml of a 1.6 *M* solution in hexane) in anhydrous benzene (200 ml) over a period of 0.5 hr. During the addition and subsequent reaction, a nitrogen atmosphere was maintained. The reaction temperature was maintained at approximately 15°. Stirring was continued for 75 min after addition of the phosphonium salt had been completed.

To the resultant orange-yellow mixture was added 2,3,4,5,6-pentafluorobenzoyl chloride in benzene (3.6 g in 40 ml of benzene, 0.0156 mole) dropwise over a period of 1.5 hr. After 15 min of additional stirring, the reaction mixture was filtered and the solid residue was washed three times with hot benzene. Although quantitative amounts of crude salts were recovered, attempted recrystallization of the residue from ethanol–ethyl acetate failed. The benzene was stripped off, leaving a yellowish solid (11 g). Recrystallization from ethyl acetate gave white crystals, mp 245–246°, and a yield of 7.4 g (74%, based on acid chloride) of α-2,3,4,5,6-pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane.

Preparation of 2,3,4,5,6-Pentafluorodiphenylacetylene (II).—α-2,3,4,5,6-Pentafluorobenzoylbenzylidenetriphenylphosphorane (1.0 g, 0.00183 mole) was heated in a small sublimation apparatus at 310° (10 mm) with an air bath as the heating source until the formation of the solid on the cold finger had ceased (approximately 1 hr). Recrystallization of the resulting solid from 95% ethanol gave 0.46 g (94%) of white needles, mp 108.5–109.5°. The infrared spectrum of this material revealed $\nu_{\max}^{CCl_4}$ 2240 (w), 1520 (s), 1500 (s), 1450 (w), 1380 (w), 1120 (m), 1030 (w), 1000 (s), and 970 (s) cm^{-1}. The absorption at 2240 cm^{-1} is attributed to weak carbon–carbon triple-bond stretching found in unsymmetrical disubstituted acetylenes. The absorption at 1450, 1500, and 1520 cm^{-1} is assigned to the fluoroaromatic ring, while the absorption at 1000 cm^{-1} is associated with C-F absorption. The pmr spectrum of the product (in deuteriochloroform) showed a multiplet centered at τ 2.7.

---

(3) J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, 3719 (1961).

(4) R. J. Harper, Jr., E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964).

Anal. Calcd for $C_{14}H_5F_5$: F, 35.42; mol wt, 268. Found: F, 36.43; mol wt, 260 (osmometry in benzene).

Preparation of Bis(pentafluorophenyl)acetylene (I).—α-2,3,4,5,6-Pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane (1.0 g, 0.00157 mole) was heated at 310° (10 mm) as described above to give 0.53 g (95%) of a flocculent white precipitate, mp 122–123° (sublimation). The infrared spectrum of this material revealed the absence of C–C triple-bond absorption in the 2200-cm^{-1} region, as expected. The product failed to show any pmr absorption.

Anal. Calcd for $C_{14}F_{10}$: F, 53.04; mol wt, 358. Found: F, 52.95; mol wt, 354 (osmometry in benzene).

Preparation of Copper Phenylacetylide.—Copper phenylacetylide was prepared by a method described previously.[2]

Preparation of II.—To a 250-ml, three-necked flask, equipped with a nitrogen inlet, a reflux condenser connected to a mercury trap, and a magnetic stirring bar, were added 3.6 g (0.022 mole) of cuprous phenylacetylide and 80 ml of dimethylformamide (DMF). The flask and contents were thoroughly flushed with nitrogen with stirring. Under nitrogen, 6.5 g (0.023 mole) of iodopentafluorobenzene in 20 ml of DMF were added. The contents were stirred and warmed in an oil bath at 140° for 15 hr. The reaction mixture turned dark. The mixture was cooled filtered, placed on a rotatory evaporator, and concentrated to dryness. The black tarlike material was dissolved in 95% ethanol and crystals formed after the flask was stored in a refrigerator. The first recrystallization from ethanol gave 1.65 g (20%) of the crude acetylene. The infrared spectrum was identical with that of an authentic sample of II. Optimum conditions for the synthesis of the acetylene were not worked out. It was found, however, that longer reaction times and higher temperatures produced a more impure product.

Preparation of Hexaarylbenzenes.—Tetraphenylcyclopentadienone (0.5 g, 0.0013 mole) and the appropriate acetylene (for II, 0.75 g, 0.0028 mole; for I, 1 g, 0.0028 mole) were placed in a 25 × 150 mm test tube and heated with the flame from a microburner. The excess acetylene was removed with a cold finger. The residue, upon cooling, was recrystallized from diphenyl ether to yield off-white crystals. The melting points of the products could not be determined since they were above 300°. The yield for both hexaarylbenzenes was 60%. The infrared spectra were consistent with polysubstituted benzenes and showed no carbonyl stretching band in either case and no C≡C band in the case of the unsymmetrical acetylene.

Anal. Calcd for $C_{42}H_{25}F_5$: C, 80.75; H, 4.03. Found: C, 80.83; H, 4.06. Calcd for $C_{42}H_{20}F_{10}$: C, 70.59; H, 2.82. Found: C, 70.98; H, 2.91.

Registry No.—I, 13557-43-2; II, 13509-88-1; benzyltriphenylphosphonium bromide, 1449-46-3; 2,3,4,5,6-pentafluorobenzyl bromide, 1765-40-8; 2,3,4,5,6-pentafluorobenzyltriphenylphosphonium bromide, 13509-91-6; pentafluorobenzoyl chloride, 653-35-0; α-2,3,4,5,6-pentafluorobenzoylbenzylidenetriphenylphosphorane, 13509-92-7; α-2,3,4,5,6-pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane, 13557-45-4; III, 13509-98-3; IV, 13509-99-4.

Acknowledgment.—The authors wish to express their gratitude to the National Institutes of Health for financial support of this research under Grant GM-12146.

Selective Demethylation of Deoxyanisoin. Mass Spectra of the Products

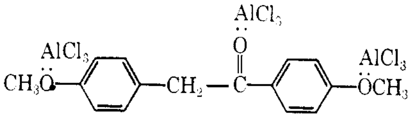
D. LEDNICER AND M. F. GROSTIC

Biochemical Research Division, The Upjohn Company,
Kalamazoo, Michigan 49001

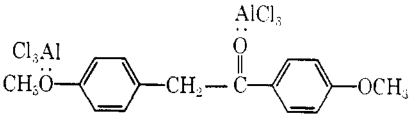
Received February 6, 1967

Recently, in connection with another problem, we had occasion to need sizable quantities of *p*-hydroxyphenyl *p*-methoxybenzyl ketone[1] (II). On the basis of previous work,[2] reaction of deoxyanisoin (I) with a limited amount of aluminum chloride would be expected to afford the desired phenol. We found, in fact, that, when deoxyanisoin was refluxed with 3 moles of aluminum chloride for 1.5 hr, the desired phenol was isolated in 30% yield accompanied by a major amount (25% by isolation) of the bisdemethylated product (III).[3] In an attempt to cut down the apparent overreaction, we cut the amount of aluminum chloride used back to 2 moles. The time required for the disappearance of starting material was in this case considerably longer (18 hr). To our surprise, the phenolic product of this reaction was not the known compound (II) but its hitherto unreported isomer (IV) (see section on mass spectra for structural proof and Scheme I).

These divergent reaction patterns can perhaps best be explained as a balance between thermodynamic and kinetic effects. Thus, the 3 moles of the Lewis acid probably complex with the three oxygens of the molecule (V). The electron-withdrawing carbonyl group *para* to the complexed ether group accelerates the rate of reaction of that group relative to the ether *para* to the methylene and leads to II. The use of an insufficient amount of aluminum chloride (2 moles) brings into play the relative basicities of the oxygens. The electron-releasing methylene group serves to render the ether *para* to that group more basic than that *para* to the carbonyl, resulting in a complex such as VI. The net effect is a reaction which, though much slower, leads to IV.



V



VI

Mass Spectra.—The isomers represented by II and IV involve a single interchange of two functional groups. Consequently, physical measurements such as the ultraviolet, infrared, or nmr spectra could not lead to unequivocal assignments of structures without some involved arguments. Mass spectrometry seemed uniquely appropriate for this structural assignment.

The partial mass spectra of compounds I–IV are shown in Table I. These data suggest fragmentation patterns for deoxyanisoin (I) and the bisdemethylated compound (III) such as those shown in Scheme II. The most intense peak in the spectrum of I (b, *m/e* 135) demonstrates the presence of a methoxyl *para* to the carbonyl group. It is of note that the analogous ion (b′) is the base peak of the spectrum of III and is observed 14 mass units lower at *m/e* 121 because the methyl group has been replaced by hydrogen.

A predominant peak at *m/e* 135 in the mass spectrum is thus diagnostic for the presence of ion b, and the presence of a methoxyl group *para* to the carbonyl

---

[1] W. Tadros, L. Ekladios, and A. B. Sakla, *J. Chem. Soc.*, 2351 (1954).

[2] T. R. Seshardri and G. B. Veukatasubramanian, *ibid.*, 1660 (1959).

[3] N. P. BuuHoi, M. Sy, and N. D. Xuong, *Bull. Chem. Soc. France*, 629 (1956).