Heteroatom Chemistry
Volume 3, Number 2, 1992

Wittig Reaction of 1-Dicyanomethyleneacenaphthen-2-one

Wafaa M. Abdou* and Neven A. F. Ganoub

National Research Centre, Dokki, Cairo, Egypt

Received 23 April 1991.

ABSTRACT

The Wittig reaction of the titled compound **2** *with alkoxycarbonylmethylenetriphenylphosphoranes* (**1a,b**) *has been investigated and the reaction products* **6**, **10**, *and* **11** *isolated and identified. On the other hand, reaction of* **2** *with benzoylmethylenetriphenylphosphorane* (**1c**) *proceeded only at high temperature, yielding* **7c** *and* **10**. *Mechanisms accounting for the formation of the adducts are discussed, and the synthetic utility of the products were tested.*

INTRODUCTION

Over the past several years, investigations have established the synthetic utility of phosphorus ylides as versatile and extremely mild alkenylating and alkylating reagents [1, 2]. Cycloaddition has, so far, not been investigated systematically. This investigation focuses on the preparation of a variety of heterocycles by reaction of the ylides **1** with α,β-unsaturated nitriles, e.g., 1-dicyanomethyleneacenaphthen-2-one (**2**). The latter compound is an attractive molecule, since it has been found, in earlier papers, that the parent compound, acenaphthenequinone, behaved differently from other related α-diketones, such as benzil or phenanthrenequinone, toward alkyl phosphites [3] or ylide phosphoranes [4]. It was deduced that a carbonyl group in **2** is more reactive than those in benzil or phenanthrenequinone [4, 5].

As a prelude to the current work, we reported [6] the action of **1** on 10-dicyanomethylene-9(10H)-phenanthrenone (**3**). The dipolar intermediate (**4**), accounted for the formation of the new ylide phosphorane adducts **5** (Scheme 1). It was also pointed out that ylides **5** can undergo common Wittig reactions with active carbonyl compounds.

RESULTS AND DISCUSSION

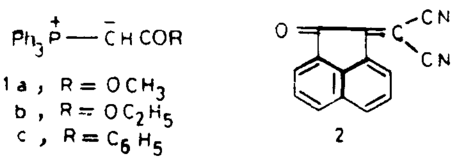
In our present systematic study, we have treated the nitrile **2** with an equimolar amount of methoxycarbonylmethylenetriphenylphosphorane (**1a**) in absolute benzene at room temperature for 48 h. The reaction mixture was separated by chromatography on silica gel, whereby, triphenylphosphine oxide, as well as three crystalline products, **6a**, **10a**, and **11** were isolated. The first product was obtained as yellow crystals in 12% yield and formulated as **6a** for the following reasons: (1) elemental and mass spectral analyses (by Field Ionization Method) for compound **6a** corresponds to an empirical formula $C_{36}H_{25}N_2O_3P$; (2) the ^{31}P-NMR spectrum shows a chemical shift, $\delta = +14.6$, that indicates a high contribution of the zwitterionic form **6** and not the ring-closed form **8** (oxaphosphorin) [7, 8]. (3) The proton of C3 in **6a** shows a P—H coupling constant of $^2J_{HP} = 17.5$ Hz at $\delta = 4.19$ in its PMR spectrum [9]. It also exhibited a signal at 4.0 (s, 3H, OCH_3). (4) The IR (cm^{-1}) spectrum of **6a** revealed the presence of strong absorption bands at 1740 (C=O, aryl ketone, for comparison, **2**: μ C=O, 1745 cm^{-1}), 1710 (C=O, ester), 2210 (CN), and 1450 cm^{-1} (P—C, phenyl).

It is also worth noting that the spectral studies of **6a** have indicated the potential formation of an

---

*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25



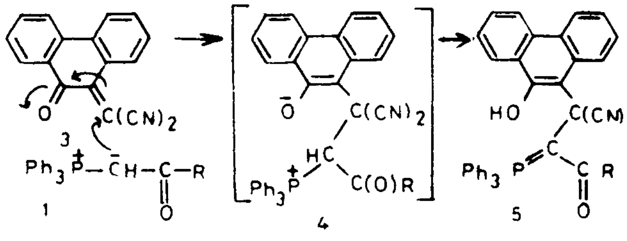
FORMULAE 1 AND 2

ylide product assigned structure **7a** on the basis of its PMR spectrum that showed, among other signals, a doublet (1H) at δ = 5.02 with a coupling constant $^4J_{HP}$ = 4.5 Hz. This doublet was ascribed to the ring methine proton of **7a**. In favor of structure **7a**, two resonances at δ = 14.6 and 22.8 appeared in the ^{31}P-NMR spectrum. The relative ratio **6a**/**7a** is 88:12.

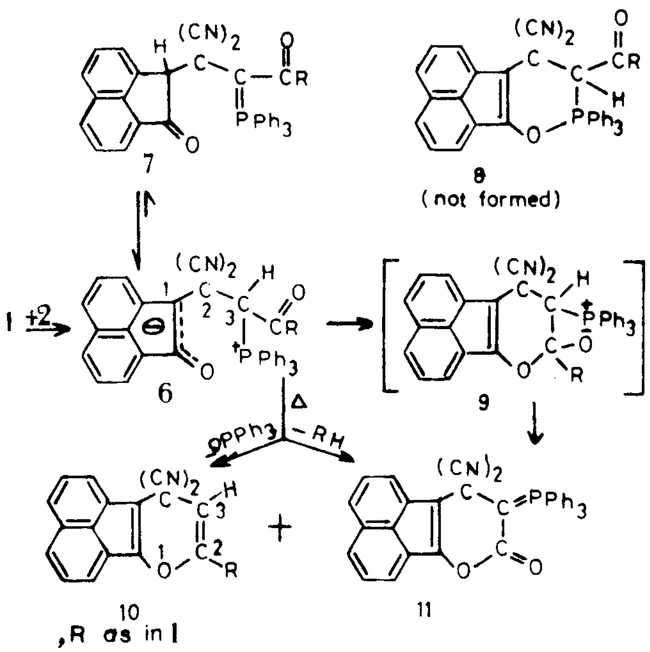
Formation of **6a** can be explained in terms of initial addition of the carbanion center in **1** to the exocyclic methide carbon in **2** (Scheme 2) to yield the zwitterion **6**. Even though compound **6a** is reasonably stable by the COR moiety (R = OCH_3), which is electron-withdrawing in nature, migration of the δ-proton to the electron rich center of the molecule also occurred to give the equilibrium **7a** $\rightleftharpoons$ **6a** (12:88, cf. ^{31}PNMR).

The second product isolated, **10a** (a yellow crystalline compound, mp 78°C, ca. 15% yield) was shown by elemental analysis and high resolution MS to possess the composition $C_{18}H_{10}N_2O_2$ (286.294, m/z = 286, M^+). Its IR (cm^{-1}) spectrum exhibited absorption bands at 2215 (CN), 1625 (C=CH) and 1100 (vinyl ether) [9]. In its ^{1}H-NMR spectrum (δ), the aromatic multiplet centered at 7.6 was integrated to 6 protons; the singlet at 6.23 (s, 1H) is attributed to the C-3 methine proton, while the pyran ring methoxyl group resonated at δ = 3.88 (s, 3H, OCH_3). In favor of the assigned structure, heating the complex ylide **6a** at 180–200°C gave **10a** and **11** accompanied by triphenylphosphine oxide (cf. Scheme 2).

Mechanistically, formation of the pyran **10** may be considered to proceed via the ring phosphorane form **9**. It is reasonable to assume that the initial dipolar structure **6**, formed from **1** and **2**, partly, was converted by an internal Wittig reaction to **10** (Scheme 2). A similar result was observed during an intramolecular Wittig olefination reaction by Sorensen [10] and others [11, 12].



SCHEME 1



The last product obtained was the major product (ca. 33% yield) consisting of brown crystals of mp 310°C and established to have the ylide structure **11** by the following physical and spectral data: (1) elemental analysis and MS support the molecular formula $C_{35}H_{21}N_2O_2P$ (532.5); accordingly, MS: m/z = 532 (M^+, 27%). (2) It showed an infrared absorption band at 1715 cm^{-1} corresponding to the $>$C=O group in pyrone. Moreover, it exhibited strong absorption frequencies at 1685 and 1505 cm^{-1} characteristic of the C=P absorption group [13], as well as around 1420 cm^{-1} for the P—C, phenyl. (3) The PMR spectrum of **11** in DMSO showed only a multiplet in the region δ, 6.76–8.68, due to the aromatic protons. (4) Supplementary evidence for the assigned ylide structure **11** has been gained from its ^{31}P-NMR spectrum (in DMSO), and it gave a positive shift at δ = 26.2, a value that falls in the range frequently recorded for this class of compounds [7, 13]. (5) The complex ylide **11** was obtained when the nitrile **2** was allowed to react with ethoxycarbonylmethylenetriphenylphosphorane **(1b)** at room temperature to give **6b**, **10b**, and **11**.

It may be considered that the lactone ylide **11** is formed by the lactonization of the dipolar ion **6a,b**, *via* the expulsion of a suitable moiety (i.e., RH, R = OCH_3, or OC_2H_5) (Scheme 2). Such an observation has been made before by Strandtmann et al. [11] for the reaction products of coumarin derivatives with phosphorus ylides of type **1a,b**. Undoubtedly, formation of **11** by thermolysis of **6a,b** is consistent with the assigned mechanism [11, 13].

In order to study the solvent effect on the course of the Wittig reaction, the reaction of **1** with **2** was carried out in several solvents of different polarity (benzene, THF, and MeOH) maintaining the general conditions as in the first experiment (cf. Table 1).

Similarly, the influence of the temperature was studied (cf. Table 1).

From the data shown in Table 1, it is obvious that nitrile **2** reacts with Wittig reagents **1a** or **1b** in nonpolar solvents to give preferentially the pyrone derivative **11** that always dominates the side products **6** and **10**. On the other hand, it has been demonstrated that the use of polar solvents and low temperature increase the stability of the dipolar species **6a,b** and diminish its conversion to **10a,b** and **11**.

In contrast to the behavior of **2** toward ylides **1a,b**, no reaction occurred when **2** was treated with benzyoylmethylenetriphenylphosphorane (**1c**) in benzene (THF or ethyl alcohol) at room temperature, and starting materials were recovered practically unchanged even after 60 h. However, carrying out the reaction in boiling benzene (best yield in ethanol, cf. Table 1), using equimolar amounts of the reactants, led to the formation of the ylide **7c**, and the pyran **10c** accompanied by triphenylphosphine oxide. The structure of the new compounds **7c** and **10c** were established from their elemental analyses and spectral properties, which are consistent with expectation (cf. experimental).

Wittig Olefination Reaction of 6a,b *and* 11

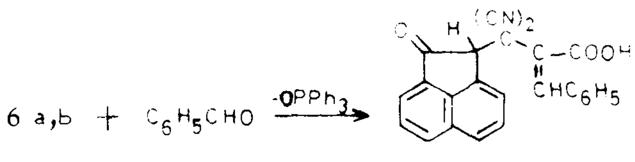
It was of interest to explore the synthetic usefulness of the alkylated phosphoranes **6a,b** and **11**. When ylides **6a,b** were allowed to react with aromatic aldehydes (e.g., C_6H_5CHO), in the presence of sodium ethoxide, the Wittig reaction occurred readily and gave the expected benzylidene derivative **12**. Because of the alkaline hydrolysis, **12** was obtained as the acid rather than as the ester. The structure of **12** was established from its elemental analysis and spectral properties (cf. Experimental), which are consistent with the assigned structure.

TABLE 1 Effect of Solvent and Temperature on the Wittig Reaction of **2**

Solvent	Temp. °C	Yield(%)^a 6a	10a	11	6b	10b	11	7c	10c
Benzene	25	12	15	33	10	8	42	—	—
	R^b	—	28	45	—	22	56	62	17
THF	25	23	18	25	23	14	31	—	—
	R	—	32	37	—	36	42	45	10
MeOH	25	35	20	16	32	25	18	—	—
	R	—	40	40	—	40	30	56	22

[a] Yields are approximated and based on the amount of the starting material (100% disappearance of **2**; TLC).

[b] Reflux temperature.



12

EQUATION 1

On the other hand, under our standard conditions, ylide **11** and benzaldehyde failed to react, even when heated at reflux in dimethyl sulphoxide or *N,N*-dimethylformamide.

CONCLUSION

The results of the present investigation showed that the initial step in the reaction of phosphorus ylides with both nitriles **3** and **2** is a carbophilic attack by the carbanion center in the Wittig reagent **1** on the most exoconjugated system to yield the phosphonium betaines **4** and **6**, respectively. However, in contrast to the behavior of **4** (not isolated) that undergoes a direct and simple Hoffmann [14] transylidation reaction yielding **5** [6], betaine **6a,b** (identified) gives stable products partly by an internal Wittig reaction and partly by lactonization to produce **10** and **11**, respectively. In this respect, the behavior of **2** is also in great disparity with that of the nonsubstituted acenaphthenequinone, which undergoes a simple Wittig reaction with the same ylide phosphoranes **1** [4].

Furthermore, the results indicate that the polarity and temperature effects play only a very limited role. Additionally, the results revealed the potential synthetic utility of the ylide **6a,b**.

EXPERIMENTAL

All melting points are uncorrected. The solvents were dried by usual techniques. Carbomethoxymethylene [15], carbethoxymethylene [15], and benzoylmethylene-triphenylphosphoranes [16] were prepared according to established procedures. The IR spectra were measured in KBr, on a Perkin-Elmer infracord Spectrometer Model 157 (Grating). The PMR spectra were run on a Varian Spectrometer at 90 MHz, using TMS as an internal reference. ^{31}P-NMR spectra were recorded, relative to external H_3PO_4 (85%), with a Varian FT-80 Spectrometer. The mass spectra were run at 70 eV on Kratos MS equipment and/or on a Varian MAT 311 A Spectrometer.

Action of Phosphorus Ylides 1a,b *on the Nitrile* 2

To a suspension of nitrile **2** [17] (2.3g, 0.01 mol) in dry benzene, (20 mL) was added a solution of ylide **1a** or **1b** (0.011 mol) in the same solvent (20 mL).

The reaction mixture was stirred at room temperature (25°C) for 48 h. The reaction mixture was then concentrated at 40 °C under reduced pressure. The solid product was redissolved in methanol (100 mL) and evaporated to dryness in the presence of silica gel (8 g). The mixture was then added to a column previously charged with silica gel in petroleum ether. The column was developed with petroleum ether containing increasing amounts of chloroform. The fraction (up to 9:1 v/v) eluted a yellow substance recrystallized from suitable solvent to give **10a** or **10b**.

Compound **10a**, yellow crystals (0.43 g, 15%), mp 78°C (cyclohexane). Anal calcd for $C_{18}H_{10}N_2O_2$ (286.294): C, 75.51; H, 3.52; N, 9.78. Found: C, 75.49; H, 3.51; N, 9.75. IR(KBr) cm^{-1}: 2215 (CN), 1625 (C═CH), and 1100 cm^{-1} (vinyl ether). ^1H-NMR ($CDCl_3$) δ, 3.88 (s, 3H, OCH_3), 6.23 (s, 1H, CH, pyran), 6.54–8.65 (m, 6H, Ar—H). MS: m/z = 286 (M^+, 18%).

Compound **10b**, yellow crystals (0.26 g, 8.8%), mp 82°C (cyclohexane). Anal calcd for $C_{19}H_{12}N_2O_2$ (300.321): C, 75.99; H, 4.03; N, 9.32. Found: C, 75.96; H, 4.01; N, 9.28. IR (KBr) cm^{-1}: 2210 (CN), 1635 (C═CH), and 1050 cm^{-1} (vinyl ether). ^1H-NMR ($CDCl_3$) δ 1.35 (t, 3H, —C—CH_3, J_{HH} = 7 Hz), 4.01 (q, 2H, CH_2) 6.1 (s, 1H, —CH, pyran), and 6.5–8.4 (m, 6H, Ar—H). MS: m/z = 300 (M^+, 15%).

The fraction (up to 8:2 v/v) afforded yellow crystals that were recrystallized from suitable solvent to give **6a** or **6b**.

Compound **6a**, yellow crystals (0.68 g, 12.2%), mp 138°C (ether). Anal calcd for $C_{36}H_{25}N_2O_3P$ (564.592): C, 76.58; H, 4.46; N, 4.95; P, 5.48. Found: C, 76.52; H, 4.44; N, 4.92; P, 5.51. IR (KBr) cm^{-1}: 2210 (CN), 1740 (C═O), 1710 (C═O, ester), and 1450 cm^{-1} (P—C, phenyl). ^1H-NMR ($CDCl_3$) δ 4.0 (s, 3H, OCH_3), 4.19 (d, 1H, CH—P, $^2J_{HP}$ = 17.5 Hz), 5.02 (d, 1H, ring methine-H of **7a**, $^4J_{HP}$ = 4.5 Hz), and 6.5–8.6 (m, 21H, Ar—H). ^{31}P-NMR ($CDCl_3$) δ = 14.6 and 22.8. MS: m/z = 564 (M^+, 5%).

Compound **6b**, yellow crystals (0.62 g, 10.7%), mp 113°C (ether). Anal calcd for $C_{37}H_{27}N_2O_3P$ (578.619): C, 76.80; H, 4.70; N, 4.84; P, 5.35. Found: C, 76.76; H, 4.68; N, 4.80; P, 5.38. IR (KBr) cm^{-1}: 2215 (CN), 1740 (C═O), 1715 (C═O, ester), and 1410 cm^{-1} (P—C, phenyl). ^1H-NMR ($CDCl_3$) δ 1.42 (t, 3H, C—CH_3, J_{HH} = 7 Hz), 4.23 (q, 2H, —CH_2—), 4.33 (d, 1H, CH—P, $^2J_{HP}$ = 18 Hz), 5.42 (d, 1H, ring methine-H of **7b** $^4J_{HP}$ = 4.5 Hz), and 6.8–8.6 (m, 21H, Ar—H). ^{31}P-NMR ($CDCl_3$) δ = 13.8 and 20.65. MS: m/z = 578 (M^+, <5%).

The fraction (up to 6:4 v/v) yielded colorless needles, mp 156°C (ca. 82% yield), of triphenylphosphine oxide [18] (mp, mixed mp, and comparative IR spectra).

The fraction (up to 4:6 v/v) gave 1.78g (33.4%) of a brown product, recrystallized from acetone to give brown material of mp 310°C and identified as the ylide **11**. Anal calcd for $C_{35}H_{21}N_2O_2P$ (532.549): C, 78.93; H, 3.97; N, 5.26; P, 5.81. Found: C, 78.90; H, 3.97; N, 5.25; P, 5.82. IR (KBr) cm^{-1}: 2225 (CN), 1715 (C═O, pyrone), 1685, and 1505 (C═P), and 1420 cm^{-1} (P—C, phenyl). ^1H-NMR (DMSO) δ 6.76–8.68 (m, 21H, Ar—H). ^{31}P-NMR (DMSO) δ = 26.2. MS: m/z = 532 (M^+, 27%).

Compound **11** was also obtained from the reaction of **1b** with **2** in 42.4% yield (mp, mixed mp, and comparative spectra).

Action of 1c *on the Nitrile* 2

A mixture of **2** (2.3 g, 0.01 mol) and ylide **1c** (3.8 g, 0.01 mol) in benzene (40 ml) was refluxed for 18 h. The reaction mixture was worked up as mentioned above. Chromatography on silica gel with pet.ether-chloroform (8:2, 6:4, 4:6) gave the products **10c**, TPPO, and **7c** in sequence.

Compound **10c**, yellow needls (0.57 g, 17.3%), mp 192°C (benzene). Anal calcd for $C_{23}H_{12}N_2O$ (332.65): C, 83.12; H 3.63; N, 8.43. Found: C, 82.09; H, 3.62; N, 8.37. IR (KBr) cm^{-1}: 2220 (CN) and 1622 (C═CH). ^1H-NMR (DMSO): δ 6.02 (s, 1H, —CH, pyrone), and 6.6–8.6 (m, 6H, Ar—H). MS: m/z = 332 (M^+).

Compound **7a** was isolated as brown crystals (3.3g, 62.5%), mp 308°C (acetone). Anal calcd for $C_{41}H_{27}N_2O_2P$ (610.663): C, 80.62; H, 4.45; N, 4.58; P, 5.07. Found: C, 80.59; H, 4.42; N, 4.56; P, 5.11. IR(KBr) cm^{-1}: 1680 and 1510 (C═P) and 1420 cm^{-1} (C—P, phenyl). ^{31}P-NMR (DMSO) δ = 24.8.

Thermal Decomposition of 6a

The ylide adduct **6a** was heated (bath temp 230°C) for one hour under reduced pressure (5 mm/Hg) in a cold-finger sublimator. The reaction vessel was left to cool and ethyl alcohol (5 mL) was added. The crystals that separated were recrystallized from ethanol to give a brown substance of mp 310°C (0.4 g, 50%) and identified as **11** (TLC, MS).

The ethanol filtrate was evaporated under reduced pressure and the residue crystallized from pentane to give yellow crystals in 8% yield, mp 78 °C and proved to be **10a** (TLC, MS).

Triphenylphosphine oxide was also isolated from the residual substance (mp, and mixed mp, and comparative IR spectra) [18].

Wittig Reaction of 2 *in Different Solvents*

In two parallel experiments, the reaction of **1** and **2** was carried out in THF and methanol (similar to the reaction of **1** with **2** in benzene), employing the same conditions. The reaction mixture was worked up in the usual way and chromatography on silica gel gave products **6**, **10**, and **11**. For comparative yields see Table 1.

Wittig Reaction of **2** *at High Temperatures*

In three parallel experiments, the reaction of **2** with **1a**, **1b**, or **1c** was carried out in boiling benzene, THF, and methanol (similar to the reaction of **1** with **2** at room temperature), employing the same amounts. Working up the individual solutions in the usual manner, **10a–c** and **11** were isolated by chromatography. For comparative yields, see Table 1.

Wittig Reaction of the Produced Ylides **6** *and* **11**

To a solution of sodium (0.2 g) dissolved in ethanol (50 ml) was added freshly distilled benzaldehyde (0.6 g, 0.006 mol), and then the ylide **6a,b** (2.8g, 0.005 mol) was added portionwise. The reaction mixture was stirred at room temperature for 10 h. The resultant reaction mixture was concentrated to 10 mL and then diluted to 50 mL with H_2O. The aqueous phase was made strongly acidic with concentrated HCl and the precipitated product was filtered off, washed with cold H_2O, and recrystallized from ethanol to give 1.0 g (53.8%) of the olefinic product **12**, mp 164–167°C. Anal calcd for $C_{24}H_{14}N_2O_3$ (378.392); C, 76.18; H, 3.73; N, 7.40. Found: C, 76.16; H, 3.70; N, 7.36. IR (KBr) cm^{-1}: 3350 (OH), 2225 (CN), and 1700 (C=O). ^{1}H-NMR: δ 4.17 (s, 1H, C—H), 6.33 (s, 1H, vinyl), 7.45 (m, 11H, Ar—H), and 10.75; (broad, 1H, OH). MS: m/z 378 (M^+).

No reaction was observed, however, in a comparable experiment, using ylide **11**, or when the reactants were refluxed in dimethyl sulphoxide or *N,N*-dimethylformamide for 20 h.

REFERENCES

[1] J. I. G. Cadogan, *Organophosphorus Reagent in Organic Synthesis*, London, Academic Press, 1979.
[2] A. W. Johnson, *Ylide Chemistry*, New York, Academic Press, 1966.
[3] F. Ramirez, *Pure and Applied Chem., 9,* 1964, 337; F. Ramirez, N. Ramanthan, *J. Org. Chem., 26,* 1961, 3041.
[4] O. Tsuge, M. Tashiro, I. Shinkai, *Bull. Chem. Soc. Japan, 42,* 1969, 181.
[5] O. Tsuge, M. Tashiro, *Bull. Chem. Soc. Japan, 36,* 1963, 970; *38,* 1965, 339; *39,* 1966, 2477.
[6] W. M. Abdou, N. A. F. Ganoub, *Chem. and Industry (London), 6,* 1991, 217.
[7] M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark, J. R. van Wazer, *Topics in Phosphorus Chemistry*, Vol. 5, Interscience Publishers, New York, 1967.
[8] S. O. Grim, W. McFarlane, T. J. Marks, *Chem. Commun.,* 1967, 1191.
[9] R. M. Silverstein, G. C. Bassler, T. C. Morril, *Spectroscopic Identification of Organic Compounds*, Wiley Inc., New York, 1981.
[10] A. K. Sorensen, N. A. Klitgaard, *Acta Chem. Scand., 24,* 1970, 343.
[11] M. von Strandtmann, M. P. Cohen, C. Puchalski, and J. Shavel, Jr., *J. Org. Chem., 33,* 1968, 4306.
[12] F. Ramirez, O. P. Madan, C. P. Smith, *J. Org. Chem., 30,* 1965, 2284; F. Ramirez, O. P. Madan, S. R. Heller, *J. Chem. Soc., 87,* 1965, 731.
[13] W. W. Sullivan, D. Ullmann, H. Shechter, *Tetrahedron Lett,* 1969, 457.
[14] H. Hoffmann, *Chem. Ber., 94,* 1961, 1331.
[15] H. J. Bestmann, O. Kratzer, *Chem. Ber., 95,* 1962, 1894.
[16] F. Ramirez, N. B. Desai, N. McKelvie, *J. Am. Chem. Soc., 84,* 1962, 1312.
[17] H. Junek, H. Hambock, B. Hornischer, *Monatsh. Chem., 98,* 1967, 70.
[18] A. Michaelis, L. Gleichmann, *Chem. Ber., 15,* 1882, 801.