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Reactions of Benzenediazonium-2-carboxylate with Arylimino- and Acylmethylenetriphenylphosphoranes

Takayuki KAWASHIMA and Naoki INAMOTO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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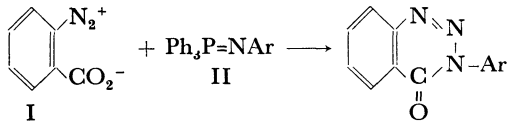
There is no report on the reaction of benzenediazonium-2-carboxylate (I) with arylimino- (II) or acylmethylenetriphenylphosphoranes (III).

The reactions of I with II gave 3-aryl-3,4-dihydrobenzo[*e*][1,2,3]triazin-4-ones (IV), *N*-arylbenzamides (V), *N*,*N'*-diarylureas (VI) and triphenylphosphine oxide (VII) in dichloromethane at room temperature, their yields being dependent upon aryl group of II (Table 1).



I + $Ph_3P{=}NAr$ (II) ⟶ IV + PhCONHAr (V) + $(ArNH)_2CO$ (VI) + Ph_3PO (VII)

a: Ar=Ph
b: Ar=*p*-MeC_6H_4
c: Ar=*p*-ClC_6H_4

TABLE 1. REACTIONS OF BENZENEDIAZONIUM-2-CARBOXYLATE (I) WITH ARYLIMINOTRIPHENYLPHOSPHORANES (II)[a]

II	Ar	IV(%)	V(%)	VI(%)	VII(%)
a	Ph	13.4	9.6	—	81.5
b	*p*-MeC_6H_4	20.0	—	4.4	90.0
c	*p*-ClC_6H_4	—	20.2	3.8	91.1

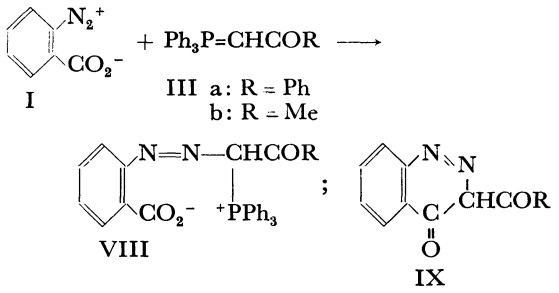
a) Yields were calculated on the basis of the amount of II used.

The products were identified by the comparison of the melting points and IR spectra with those of authentic samples and on the basis of the MS spectra.

The formation of IV is explicable by the attack of the diazonium group of I to the imino nitrogen atom of II, followed by the elimination of VII. Separate experiments indicated that benzanilide (Va) was not produced from IVa but produced quantitatively by the reaction of IIa with benzoic acid,[1] which is produced by the decomposition of I,[2] under the same condition. Urea (VI) is considered to be formed by the reaction of II with carbon dioxide, which was produced by decomposition of I, followed by the hydrolysis of isocyanate or carbodiimide thus produced during the isolation.

Variation in the yields of IV, V, and VI is attributable to a competition of the reaction between I and II with the decomposition of I to benzoic acid and carbon dioxide. For example, the absence of IVc in the case of IIc is attributable to a low nucleophilicity of the imino nitrogen in IIc because of the presence of electron-attractive *p*-chlorine atom.

Next, the reactions of I with acylmethylenetriphenylphosphoranes (III) were carried out in dichloromethane at room temperature. The products were phosphonium betaines (VIII) instead of expected IX.



I + $Ph_3P{=}CHCOR$ (III a: R = Ph, b: R = Me) ⟶ VIII ; IX

The structure of VIII was determined by the elemental analyses, the IR, ^1H-, and ^{31}P-NMR spectra. The ^{31}P-NMR spectra (δ −4.5 (in $CHCl_3$) and −3.8 (in $C_2H_4Cl_2$) from 85% phosphoric acid as external standard for VIIIa and VIIIb, respectively) support the structure of alkylidenephosphorane or phosphonium salt.[3] The IR spectra showed the absence of carboxyl group and the presence of carboxylate group (I: 1630 and 1360; VIIIa: 1595 and 1360; VIIIb: 1625 and 1360 cm^{-1}). From these data, another possible structures were ruled out.

Thermal decomposition of VIII gave VII and tarry material containing carboxyl group, instead of IX.

A reason why IX is not formed is attributable to a lack of nucleophilicity of α-carbon atom in VIII.

N-Benzoylimino- and α-benzoylbenzylidenetriphenylphosphoranes did not react with I under the same condition.

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Experimental

Materials. The following compounds were prepared by the methods described in literatures: benzenediazonium-2-carboxylate (I);[4] phenylimino- (IIa),[5] mp 128—131°C; *p*-tolylimino- (IIb),[6] mp 133—136°C; *p*-chlorophenylimino- (IIc),[6] mp 116—118°C; benzoylmethylene- (IIIa),[7] mp 181—183°C; and acetylmethylenetriphenylphosphoranes (IIIb),[8] mp 203—205°C.

Reactions of I. *a) With Phenyliminotriphenylphosphorane (IIa)*: To an excess amount of I in dichloromethane was added 4.47 g (12.7 mmol) of IIa in dichloromethane under nitrogen and the mixture was stirred at 10°C overnight. After filtration of unchanged I and removal of the solvent *in vacuo*, the residue was chromatographed on alumina to afford 0.38 g (13.4%) of IVa (with benzene–chloroform), mp 149—150°C (from benzene) (lit,[9] 150—151°C), $\nu_{C=O}$ 1660 cm^{-1}, *m/e* 223 (M^+), 2.87 g (81.5%) of triphenylphosphine oxide (VII) (with chloroform), 0.24 g (9.6%) of benzanilide (with chloroform–ether), mp 159—160°C (from methanol), and 1.274 g of red tarry material (with ethanol).

b) With p-*Tolyliminotriphenylphosphorane (IIb)*: A similar reaction using 3.66 g (10 mmol) of IIb for 5 hr gave 0.47 g (20%) of IVb, mp 142—143°C (from benzene) (lit,[10] 143°C), $\nu_{C=O}$ 1680 cm^{-1}, *m/e* 237 (M^+), 2.50 g (90%) of VII and 0.21 g (4.4%) of VIb, mp 250°C (from ethanol) (lit,[11] 256°C).

c) With p-*Chlorophenyliminotriphenylphosphorane (IIc)*: The reaction was carried out using 4.23 g (10.9 mmol) of IIc. The reaction was slow and the presence of unchanged IIc was observed even after stirring overnight. Similar treatment gave 0.51 g (20.2%) of *N*-*p*-chlorophenylbenzamide, mp 192—193°C (from benzene) (lit,[12] 187—187.5°C), 2.76 g (91.1%) of VII and 0.23 g (3.8%) of VIc, mp 300°C from ethanol) (lit,[13] 310°C).

d) With Benzoylmethylenetriphenylphosphorane (IIIa): A similar reaction was carried out using 1.3 g (3.4 mmol) of IIIa at 0°C until the presence of unchanged IIIa was not observed by tlc. After filtration of unchanged I, the solvent was removed *in vacuo* to afford 1.1 g (61.2%) of brown crystals, mp 196—197°C (decomp.) (from ethyl acetate); IR (KBr disk): 1690, 1595, 1360, and 1105 cm^{-1}; $\lambda_{max}^{CH_2Cl_2}$: 262 (ε 23,000) and 409 nm (32,000); ^{1}H-NMR ($CDCl_3$): δ 7.3—8.2 (m); ^{31}P-NMR ($CHCl_3$): δ −4.5; *m/e*: 277 (10%), 262 (39), 184 (11), 183 (37), 108 (26), 105 (100), 77 (59), and 51 (11).

Found: C, 74.84; H, 4.71; N, 5.29%. Calcd for $C_{33}H_{25}N_2O_3P$: C, 74.99, H, 4.77; N, 5.30%.

e) With Acetylmethylenetriphenylphosphorane (IIIb): Reaction of 9.3 g (29.2 mmol) of IIIb with excess amount of I finished after 15 min at 0°C. Similar treatment gave 13.0 g (95.5%) of yellow crystals, mp 192—194°C (decomp.) (from ethyl acetate); IR (KBr disk): 1695, 1625, 1360, and 1110 cm^{-1}; $\lambda_{max}^{CH_2Cl_2}$: 258 (ε 18,000) and 398 nm (25,000); ^{1}H-NMR ($CDCl_3$): δ 2.61 (3H, s, $COCH_3$) and 7.0—7.8 (20H, m, Ph, and $-CH\langle$); ^{31}P-NMR ($C_2H_4Cl_2$): δ −3.8; *m/e*: 277 (10%), 263 (14), 262 (84), 261 (20), 185 (10), 184 (27). 183 (100), 152 (16), 133 (20), 108 (70), 107 (27), 77 (45), 52 (43), 51 (45), and 43 (39).

Found: C, 72.05; H, 4.83; N, 6.02%. Calcd for $C_{28}H_{23}N_2O_3P$: C, 72.10; H, 4.97; N, 6.01%.

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