97858-80-5; **7**, 97858-70-3; **9**, 97858-82-7; **11**, 97858-71-4; **12**, 97858-72-5; **13**, 70981-37-2; **13** (tosylate), 97764-92-6; **14**, 97858-83-8; **15**, 83829-13-4; **16**, 97858-74-7; **17**, 97858-75-8; **18**, 97858-73-6; **19**, 97858-77-0; **20**, 97764-88-0; (*E*)-**21**, 97764-87-9; (*Z*)-**21**, 97858-76-9; **22**, 97764-90-4; **23**, 97858-79-2; (*E*)-**24**, 97764-89-1; (*Z*)-**24**, 97858-78-1; **25**, 97858-81-6; **26**, 97858-84-9; **27**, 97764-99-3; **28**, 97858-90-7; **29**, 97764-98-2; **30**, 97782-01-9; (±)-**31**, 97764-93-7; (±)-**31** (ketal), 97764-95-9; (±)-**33**, 97764-96-0; (±)-**34**, 97858-85-0; **34a**, 70981-38-3; **34b**, 70919-54-9; (±)-**35**, 97764-97-1; **35a**, 97858-87-2; **35b**, 97858-89-4; **36a**, 70919-50-5; **36b**, 70981-32-7; **37**, 97782-00-8; **38**, 21592-98-3; (+)-(*S*)-MTPA-Cl, 20445-33-4; $(C_6H_5)_3PCH_3^+I^-$, 2065-66-9; $(C_6H_5)_3PCH_2CH_3^+I^-$, 4736-60-1; $(C_6H_5)_3P(CH_2)_5CH_3^+I^-$, 60106-53-8; $HO(CH_2)_2OH$, 107-21-1; Br_2, 7726-95-6; *trans*-ClCH=CHCl, 156-60-5; *n*-BuSH, 109-79-5; cyclohexanone, 108-94-1; (±)-1,1-(ethylenedioxy)-2-bromocyclohexane, 97764-94-8; 1,1-(ethylenedioxy)-2-cyclohexene, 1004-58-6; 2-cyclohexenone, 930-68-7; 2,2-(ethylenedioxy)-7,8-dichlorobicyclo[4.2.0]octane, 2018-82-8; phthalic anhydride, 85-44-9; *d*-α-(1-naphthyl)ethylamine, 3886-70-2; 4(a)-methyl-2-adamantanone, 88494-22-8; 4(e)-methyl-2-adamantanone, 19301-60-1; 4(a)-hydroxy-2-adamantanone, 27863-77-0; bicyclo[3.2.1]octan-8-one, 55679-31-7.

Reaction of Nucleophiles with 1,1-Dinitro-2,2-diphenylethylene[1]

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Products of the reaction of a variety of nucleophiles with $Ph_2C{=}C(NO_2)_2$ are reported. Michael-type adducts have been isolated: ($Ph_2C(N)CH(NO_2)_2$) for $N^- = (RO)_2PO^-$, $(RO)_2PS^-$, $RCOCH_2^-$. With the nucleophiles MeO^- or $Me_2C{=}NO_2^-$ in Me_2SO the adducts are formed but are hydrolyzed upon workup with 5% aqueous HCl at 25 °C to yield benzophenone. Benzophenone is also the major product from reaction with the nucleophiles NO_2^-, AcO^-, $MeC({=}S)O^-$, EtO^-, and Me_3CO^- in Me_2SO. With $N^- = Me_3CS^-$, ArS^-, PhO^-, or $PhSe^-$ in Me_2SO, vinylic substitution occurs to yield $Ph_2C{=}C(N)NO_2$. With $ArSO_2^-$ in DMF nucleophilic aromatic substitution occurs to yield *p*-$ArSO_2C_6H_4COPh$.

We have found that 1,1-dinitro-2,2-diphenylethylene (**1**) undergoes a variety of reactions with nucleophiles. We originally thought that **1** might undergo vinylic substitution by an electron-transfer process[2,3] similar to the $S_{RN}1$ reaction which occurs for 2,2-dinitropropane[4,5] and other 2-substituted 2-nitro alkanes.[6,7] Depending upon the nucleophile and solvent, we have observed either the formation of an isolable Michael-type adduct (**2**), benzophenone, the vinyl substitution product (**3**), or the aromatic substitution product (**4**). Yields of these products are summarized in Table I. We believe these products are all formed from the initial Michael-type anion $\mathbf{2}^-$ (Scheme I). The reactions leading to the substitution products **3** or **4** were uneffected by light or free-radical inhibitors such as $(t\text{-}Bu)_2NO\cdot$, and appear to be ionic rather than electron-transfer processes.

The hydrolysis of **1** to $Ph_2C{=}O$ in the presence of base is a well-studied process involving $\mathbf{2}^-$ (N = OH) as an intermediate.[8] We have utilized a hydrolytic workup procedure involving treatment of the reaction mixture with brine followed by ether extraction wherein the hydrolysis of **1** was negligible and recovered yields of **1** of 97–98% could be isolated in the absence of added nucleophiles with Me_2SO, DMF, THF, MeOH or EtOH as solvents or with "nonreacting" nucleophiles such as NO_3^-, N_3^-, or SCN^- in Me_2SO or $(EtO_2C)_2CR^-$ in THF (Table I).

The Michael-type adducts (**2**) with N = $(MeO)_2P({=}O)$, $(EtO)_2P({=}O)$, $(MeO)_2P({=}S)$, $(EtO)_2P({=}S)$, $MeSO_2CH_2$, or $MeSOCH_2$ were isolated from Me_2SO solution while the adducts **2** with N = $MeCOCH_2$, Me_3CCOCH_2, or $PhCOCH_2$ were prepared from lithium enolates in THF. The adducts with N = CN or MeO were prepared in EtOH and MeOH, respectively. Evidence for the adduct with N = $Me_2C{=}N(O)O$ is indirect and is based upon the fact that hydrolysis of the reaction product in Me_2SO with 5% aqueous HCl yielded benzophenone, whereas workup with a brine solution yielded recovered **1**. The adduct **2l** or the anion $\mathbf{2l}^-$ apparently reverts to **1** upon hydrolysis with the brine solution but can be converted by mineral acids to $Ph_2C(OH)CH(NO_2)_2$ which decomposes to yield $Ph_2C{=}O$. Other "nonreacting" anions such as $(EtO_2C)_2CMe^-$, $(MeO_2C)_2CH^-$, or $(i\text{-}Pr)_2N^-$ may also form reversibly the anion $\mathbf{2}^-$ which upon hydrolysis reverts to **1** with protonation of N^- rather than $\mathbf{2}^-$.

Hydrolysis of **2** to yield benzophenone also occurs with **2j** (N = MeO). Treatment of the reaction product of **1** and excess MeO^- in MeOH with 5% aqueous HCl at 25 °C yielded only a mixture of $Ph_2C{=}O$ (14%) and $Ph_2C(OMe)_2$ (61%). However, acidification in a dry ice–acetone bath followed by extraction yielded 42% of **2j**[9] and 26% of $Ph_2C{=}O$. Treatment of the reaction product of **1** with 1 equiv of MeO^- with a brine workup also yielded mainly $Ph_2C{=}O$ (73%) but in this case a low yield of the substitution product, **3j** (7%), was also detected.

Benzophenone was the major product with oxygen nu-

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[1] This work was supported by Grant CHE-8119343 from the National Science Foundation.

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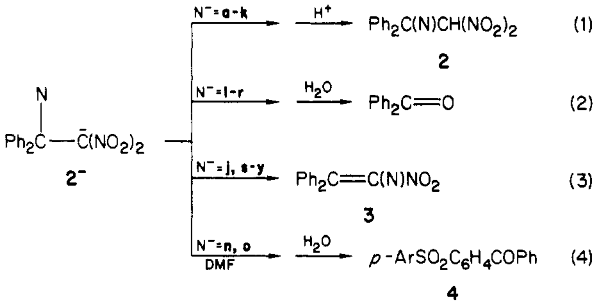
Table I. Reaction of $Ph_2C{=}C(NO_2)_2$ (1) with Nucleophiles (N^-) in Me_2SO[a]

		yield, %[b]			
N^-	time, h; temp, °C	recovered 1	$Ph_2C(N)CH(NO_2)_2$ (**2**)	$Ph_2C{=}C(N)NO_2$ (**3**)	$Ph_2C{=}O$
$(MeO)_2P(=O)^-$	0.5; 25	14 (GC)	75 (I)	0	0
$(EtO)_2P(=O)^-$	0.5; 25	22 (GC)	69 (I)	0	0
$(MeO)_2P(=S)^-$	0.5; 25	17 (GC)	65 (I), 87 (NMR)	0	0
$(EtO_2)P(=S)^-$	0.5; 25	++ (GC)	74 (NMR)	0	0
$Me_3CC(OLi){=}CH_2$ (THF)	$\sim$1; −78 to 25	33 (GC)	42 (I), 57 (NMR)	0	0
$MeC(OLi){=}CH_2$ (THF)	$\sim$1; −78 to 25	28 (GC)	51 (I), 63 (NMR)	0	0
$PhC(OLi){=}CH_2$ (THF)	$\sim$1; −78 to 25	++ (GC)	64 (NMR)	0	0
CN^-	24; 25	92 (I)	0	0	0
CN^- (EtOH)[c]	0.5; 60	8 (I)	60 (I), 83 (NMR)	0	0
MeO^-	48; 25	4 (GC)	0	7 (NMR)	73 (I)
MeO^- (MeOH)[c]	0.5; 25	0	0,[d] 42 (I)[e]	0	14 (GC),[d] 26 (GC)[e]
$MeSO_2CH_2^-$	0.5; −78 to 25	19 (GC)	63 (NMR)	0	3 (GC)
$MeSOCH_2^-$	0.5; −78 to 25	44 (GC)	42 (NMR)	0	0
Me_3CS^-	1; 25	0	0	32 (I), 76 (GC)	20 (GC)
p-$ClC_6H_4S^-$	1; 25	0	0	68 (I); 79 (GC)	12 (GC)
p-$MeC_6H_4S^-$	1; 25	0	0	87 (I), 94 (GC)	0 (GC)
Me_3CO^-	1; 25	1 (GC)	0	0	91 (I)
p-$O_2NC_6H_4S^-$	1; 25	8 (GC)	0	47 (I), 52 (GC)	31 (GC)
PhS^-	1; 25	0	0	85 (I), 97 (GC)	2 (GC)
$PhSe^-$	1; 25	0	0	48 (I), 62 (GC)	31 (GC)
PhO^-	36; 25	0	0	49 (I), 67 (GC)	31 (GC)
p-$MeOC_6H_4O^-$	48; 25	4 (GC)	0	0 (GC)	86 (GC)
p-$O_2NC_6H_4O^-$	48; 25	90 (I)	0	0 (GC)	3 (GC)
$MeCO_2^-$	12; 25	74 (I)	0	0	19 (GC)
$MeC(=S)O^-$	12; 25	67 (I)	0	0	21 (GC)
NO_2^-	3; 25	0	0	0	94 (I)
EtO^-	1; 25	4 (I)	0	0	83 (I)
HO^-	1; 25	0	0	0	96 (I)
$PhSO_2^-$	24; 25	5 (I)	0	0	74 (I)[f]
p-$MeC_6H_4SO_2^-$	24; 25	2 (I)	0	0	68 (I)[g]
SCN^-	36; 25	96 (I)	0	0	1 (GC)
SCN^- (EtOH)[e]	0.5; 60	90 (I)	0	0	0
$Me_2C{=}NO_2^-$	14; 25	92 (I)	0	0	0[h]
NO_3^-	40; 25	95 (I)	0	0	2 (GC)
N_3^-	24; 25	96 (I)	0	0	1 (GC)
$(i\text{-}Pr)_2N^-Li^+$ (THF)	$\sim$1; −78 to 25	96 (I)	0	0	0
$(EtO_2C)_2CMe^-Li^+$ (THF)	$\sim$1; −78 to 25	94 (GC)	0	0	0
$(MeO_2C)_2CH^-Li^+$ (THF)	$\sim$1; −78 to 25	97 (GC)	0	0	0

[a] Typical reactions on a 2-mmol scale involved a 1:1 ratio of 1 and K^+N^- ($\sim$0.05 M) under N_2 which was poured into brine from which reaction products were extracted. [b] I, isolated yield; NMR, ^1H NMR yield with internal standard; GC, GLC yield with internal standard. [c] Ratio of N^-:1 = 13. [d] Upon treatment of reaction product with 5% aqueous HCl at 25 °C; a 61% yield of $Ph_2C(OMe)_2$ was also isolated. [e] Acidification at dry ice–acetone temp. [f] In DMF a 21% yield of p-$PhSO_2C_6H_4COPh$ was isolated. [g] In DMF a 22% yield of p-(p-$MeC_6H_4SO_2)C_6H_4COPh$ was isolated. [h] Acidification by 5% aqueous HCl gave an 88% yield of Ph_2CO.

Scheme I



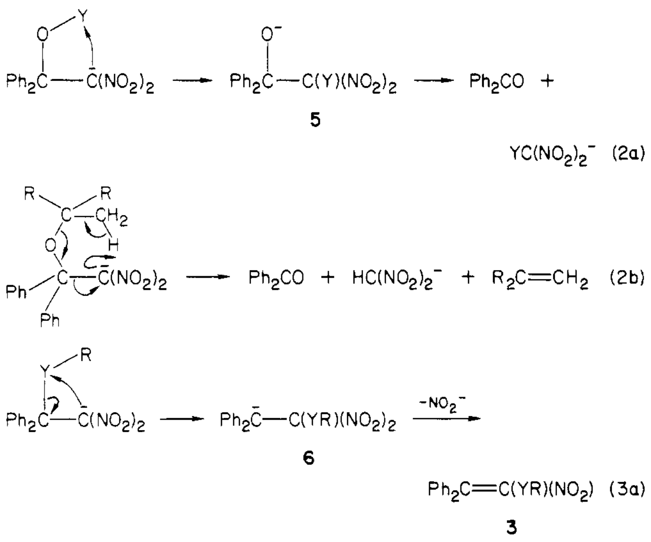
a, $(MeO)_2PO^-$
b, $(EtO)_2PO^-$
c, $(MeO)_2PS^-$
d, $(EtO)_2PS^-$
e, $MeCOCH_2^-$
f, $Me_3CCOCH_2^-$
g, $PhCOCH_2^-$
h, $MeSO_2CH_2^-$
i, $MeSOCH_2^-$
j, MeO^-
k, CN^-
l, $Me_2C{=}NO_2^-$
m, NO_2^-
n, $PhSO_2^-$
o, p-$MeC_6H_4SO_2^-$
p, $MeCO_2^-$
q, $MeC(=S)O^-$
r, t-BuO^-, EtO^-
s, t-BuS^-
t, PhS^-
u, p-$ClC_6H_4S^-$
v, p-$O_2NC_6H_4S^-$
w, p-$MeC_6H_4S^-$
x, $PhSe^-$
y, PhO^-
z, p-$MeOC_6H_4O^-$

cleophiles such as NO_2^-, $ArSO_2^-$, $MeCO_2^-$, MeC(=S), EtO^-, or Me_3CO^- in Me_2SO solution. With these nucleophiles **2** may undergo hydrolysis during workup. However, there is a possibility that $\mathbf{2}^-$ undergoes intramolecular reactions prior to hydrolytic workup since there was no evidence of the formation of the Michael-type adducts **2m–q** by ^1H NMR or GLC of the crude reaction products.

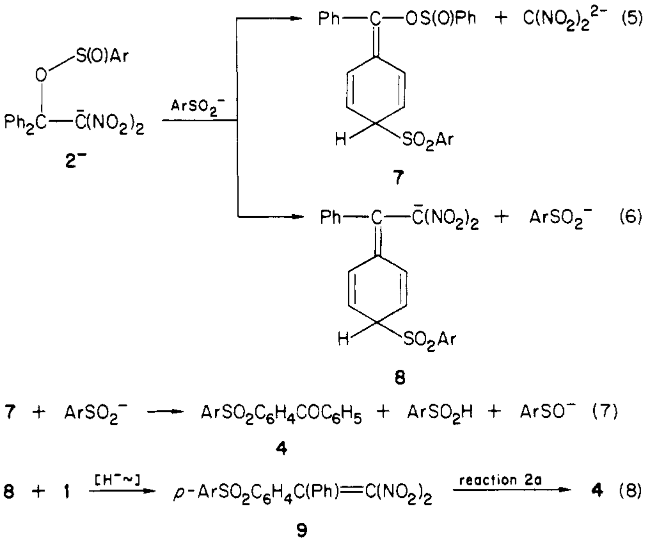
Among the possible unimolecular reactions that $\mathbf{2}^-$ can undergo are reactions 2a, 2b, and 3a (Scheme II). Reaction 2a with Y = NO, ArSO, MeCO, or MeCS or reaction 2b with R = H or Me may be involved in the formation of Ph_2CO with nucleophiles **m–r** in Me_2SO solution. With MeO^- in Me_2SO, the vinyl substitution product (**3j**) was observed in low yield, whereas with EtO^- or Me_3CO^- in Me_2SO, vinylic substitution products were not observed although it seems reasonable that these products would have survived the hydrolytic workup. This lends support to the postulation of reaction 2b when the alkoxide ion contains a β-hydrogen atom.

Vinyl substitution (reaction 3) became the predominant reaction with N^- = ArS^-, $PhSe^-$, or PhO^- in Me_2SO solution. With these nucleophiles, reactions 2a or 2b cannot occur. Reaction 3a now becomes a possibility. Alternately, these nucleophiles may add reversibly to **1**. This allows the possibility of the formation of the kinetically and thermodynamically less favorable anion **6** which would readily eliminate NO_2^-. It seems possible that the direct formation of **6** from **1** might have an unfavorable energy of activation which might be overcome by the unimolecular rearrangement of $\mathbf{2}^-$ to **6**. Process 3 was observed for p-$XC_6H_4S^-$ with X = NO_2, Cl, H, or Me with the yield of **3**

Scheme II



Scheme III



increasing with the basicity of the anion ($NO_2 < Cl < H$, Me). With p-$XC_6H_4O^-$, no reaction was observed with X = NO_2, a 67% yield of **3y** was obtained with X = H, and only $Ph_2C{=}O$ was observed with X = p-MeO. In the latter case perhaps reaction 3 occurred readily but the resulting p-anisyl vinyl ether (**3z**) was hydrolyzed during workup. Qualitatively we have observed in dioxane–H_2O mixtures that Ph_2CO is formed more rapidly from $Ph_2C{=}C(OPh)NO_2$ than from $Ph_2C{=}C(SPh)NO_2$. Presumably these hydrolyses reactions involve initial protonations at the oxygen or sulfur atoms, a process which would be much enhanced for the p-anisyl derivative **3z**.

Reaction 3 occurred for Me_3CS^- although a 20% yield of Ph_2CO was also observed. There was no indication of the formation of Ph_2CS, the product expected from reaction 2b.

Vinyl substitution products analogous to **3** have been previously observed in the reactions of 9-(nitromethylene)fluorene with CN^- and MeO^- in Me_2SO, whereas the Michael-type adducts are formed with these anions and 9-(dinitromethylene)fluorene.[10]

Reaction of **1** in Me_2SO solution with $PhSO_2^-$ or p-$MeC_6H_4SO_2^-$ yielded only Ph_2CO, possibly via reaction 2a. However, in DMF solution these nucleophiles also produced the products of nucleophilic aromatic substitution (**4**), products which are not formed from the reaction of $ArSO_2^-$ with Ph_2CO. Aromatic substitution products were not observed with any of the other nucleophiles studied including mercaptide or thiophenoxide anions. However, the other nucleophiles were not studied in DMF solution where reaction 4 was observed with $N^- = ArSO_2^-$. The anion $\mathbf{2}^-$ with N = ArS(O)O may undergo reaction 2a slowly and thus allow a second nucleophilic attack to occur with elimination of an α-substituent. Two possibilities are shown in Scheme III. Reaction 5 involves the elimination of the dianion $C(NO_2)_2^{2-}$ and leads to the intermediate **7** which could undergo the elimination reaction 7 leading directly to **4**. However, reaction 6 is perhaps more reasonable. Intermediate **8** could be formed from either $\mathbf{2}^-$ or directly from **1**. Hydride transfer from **8** to **1**, or perhaps to the solvent DMF, could yield **9** which could now participate in reaction 2a. Studies are being initiated to elucidate the mechanism of this surprising nucleophile aromatic substitution reaction and to investigate its possible extensions to other nucleophiles.

Experimental Section

General Procedures. Solutions of nucleophiles (~0.05 M) were prepated in Me_2SO under N_2 by reaction of Me_3COK with the conjugate acid of **a–d**, **h**, **s–z**. The dimsylate anion (**i**) was prepared from KH while lithium enolates (**e–g**) were prepared in THF by reaction with $(i\text{-}Pr)_2NLi$. Dry salts of the other anions were dissolved in Me_2SO. 1,1-Dinitro-2,2-diphenylethylene[11] in 10 mL of the solvent was added to give a reaction mixture 0.05 M in each reagent. After reaction, the mixture was poured into 75 mL of brine and extracted with ether (3 × 50 mL). The ether solutions were washed with water and brine solutions, dried ($MgSO_4$), and evaporated to yield residues which were analyzed by GC and ^1H NMR, or recrystallized from methanol to yield isolated products. For the isolation of **2a–d**, the brine solutions were acidified with 5% aqueous HCl before ether extraction. For the isolation of **2e–g**, the THF was removed under vacuum before hydrolysis, and the residue suspended in Et_2O and neutralized with 5% aqueous HCl.

1-Nitro-1-(phenylthio)-2,2-diphenylethylene (3t): mp 152–153 °C. Anal. Calcd for $C_{20}H_{15}NO_2S$: 333.08236; C, 72.05; H, 4.54; N, 4.20; S, 9.61. Found: *m/e* 333.0818; C, 71.81; H, 4.63; N, 4.27; S, 9.45.

1-Nitro-1-[(*p*-chlorophenyl)thio]-2,2-diphenylethylene (3u): mp 151–152 °C. Calcd for $C_{20}H_{14}ClNO_2S$: 367.04338. Found: *m/e* 367.04396.

1-Nitro-1-[(*p*-nitrophenyl)thio]-2,2-diphenylethylene (3v): mp 137–138 °C. Calcd for $C_{20}H_{14}N_2O_4S$: 378.06743. Found: *m/e* 378.06875.

1-Nitro-1-[(*p*-methylphenyl)thio]-2,2-diphenylethylene (3w): mp 162–163 °C. Calcd for $C_{21}H_{17}NO_2S$: 347.09801. Found: *m/e* 347.09939.

1-Nitro-1-(phenylseleno)-2,2-diphenylethylene (3x): orange needles, mp 138–139.5 °C. Anal. Calcd for $C_{20}H_{15}NO_2Se$: 381.02680; C, 63.16; H, 3.97; N, 3.68; Se, 20.76. Found: *m/e* 381.02643; C, 62.98; H, 3.92; N. 3.55; Se, 20.56.

1-Nitro-1-phenoxy-2,2-diphenylethylene (3y): mp 136.5–137.5 °C. Anal. Calcd for $C_{20}H_{15}NO_3$: 317.10520; C, 75.70; H, 4.76; N, 4.41. Found: *m/e* 317.10497; C, 75.92; H, 4.77; N, 4.36.

1-Nitro-1-(*tert*-butylthio)-2,2-diphenylethylene (3s): mp 118–119 °C. Anal. Calcd for $C_{18}H_{19}NO_2S$: 313.11366, C, 68.98; H, 6.11; S, 10.22; N, 4.46. Found: *m/e* 313.11313; C, 68.83; H, 5.99; S, 10.05; N, 4.70.

1-Nitro-1-(phenylsulfinyl)-2,2-diphenylethylene. Oxidation of **3t** with 1 equiv of p-$ClC_6H_4SO_3H$ for 12 h at 25 °C gave the sulfoxide (94%), mp 187.5–189 °C, from ethyl acetate. Anal. Calcd for $C_{20}H_{15}NO_3S$: 349.07728; C, 68.75; H, 4.33; N, 4.01; S, 9.18. Found: *m/e* 349.07712; C, 68.46; H, 4.33; N, 4.02; S, 9.39.

1-Nitro-1-(phenylsulfonyl)-2,2-diphenylethylene. Oxida-

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J. Org. Chem. 1985, 50, 3881-3884 3881

tion of **3t** with 2 equiv of 30% H_2O_2 for 12 h at 25 °C yielded the sulfone (65%), mp 200.5–202 °C, from ethyl acetate. Anal. Calcd for $C_{20}H_{15}NO_4S$: 365.07219; C, 65.74; H, 4.14; N, 3.83; S, 8.77. Found: *m/e* 365.07228; C, 65.75; H, 4.14; N, 3.82; S, 8.82.

***p*-[(*p*-Methylphenyl)sulfonyl]benzophenone.** Reaction of **1** (2.56 mmol) with *p*-$MeC_6H_4SO_2Na{\cdot}2H_2O$ (2.56 mmol) in 30 mL of DMF for 12 h at 25 °C gave a black solution. Treatment with brine and ether extraction gave 0.15 g (22%) of the keto sulfone: mp 199–200 °C; IR (KBr) 1650, 1595, 1395, 1320, 1290, 1160, 1100, 750, 690, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06–7.27 (m, 13 H), 2.42 (s, 3 H). Anal. Calcd for $C_{20}H_{16}O_3S$: 336.08202; C, 71.41; H, 4.79; S, 9.53. Found: *m/e* 336.08180; C, 71.33; H, 4.88; S, 9.69.

***p*-(Phenylsulfonyl)benzophenone**: mp 142.5–143.5 °C; IR (KBr) 1645, 1445, 1390, 1315, 1290, 1155, 1100, 745, 705, 685 cm^{-1}. Calcd for $C_{19}H_{14}O_3S$: 322.06637. Found: *m/e* 322.06493.

1,1-Diphenyl-1-[(dimethoxy)phosphinyl]-2,2-dinitroethane (2a): mp 133 °C dec; IR (KBr) 3050, 2990, 1595, 1580, 1510, 1450, 1375, 1330, 1255, 1060, 1040, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.05 (m, 10 H), 3.46 (d, 6 H, J_{P-H} = 11.5 Hz), 7.73 (d, 1 H, J_{P-H} = 11 Hz). Calcd for $C_{16}H_{17}N_2O_7P$: 380.07735. Found: *m/e* 380.07706.

1,1-Diphenyl-1-(diethoxyphosphinyl)-2,2-dinitroethane (2b): mp 128–129 °C dec. Anal. Calcd for $C_{18}H_{21}N_2O_7P$: 408.10865; C, 52.94; H, 5.18; N, 6.86; P, 7.58. Found: *m/e* 408.10817; C, 53.7; H, 5.46; N, 6.88; P, 7.57.

1,1-Diphenyl-1-(dimethoxythiophosphinyl)-2,2-dinitroethane (2c): mp 137 °C dec. Calcd for $C_{16}H_{17}N_2O_6PS$: 396.05450. Found: *m/e* 396.05548.

4,4-Diphenyl-5,5-dinitro-2-pentanone (2e): mp 137 °C; ^1H NMR ($CDCl_3$) δ 8.18 (s, 1 H), 7.1 (s, 10 H), 3.52 (s, 2 H), 1.69 (s, 3 H). Anal. Calcd for $C_{17}H_{16}N_2O_5$: 328.10593; C, 62.19; H, 4.91; N, 8.53. Found: *m/e* 328.10540; C, 61.99; H, 5.11; N, 8.40.

2,2-Dimethyl-5,5-diphenyl-6,6-dinitro-3-hexanone (2f): mp 146–147 °C; ^1H NMR ($CDCl_3$) δ 8.52 (s, 1 H), 7.17 (s, 10 H), 3.63 (s, 2 H), 0.76 (s, 9 H). Anal. Calcd for $C_{20}H_{22}N_2O_5$: 370.15288; C, 64.85; H, 5.98; N, 7.56. Found: *m/e* 370.15268; C, 65.05; H, 5.98; N, 7.54.

Registry No. **1**, 15795-74-1; **2a**, 97807-29-9; **2b**, 97807-30-2; **2c**, 97807-31-3; **2d**, 97807-32-4; **2e**, 97807-34-6; **2f**, 97807-33-5; **2g**, 97807-35-7; **2h**, 97807-37-9; **2i**, 97807-38-0; **2j**, 97807-36-8; **2k**, 38554-49-3; **3s**, 97807-39-1; **3t**, 97807-43-7; **3u**, 97807-40-4; **3v**, 97807-42-6; **3w**, 97807-41-5; **3x**, 97807-44-8; **3y**, 97807-45-9; **a**·K, 54057-98-6; **b**·K, 54058-00-3; **c**·K, 80866-15-5; **d**·K, 71774-85-1; **e**·Li, 62415-84-3; **f**·Li, 70367-67-8; **g**·Li, 55905-98-1; **h**·K, 82101-71-1; **i**·K, 15590-26-8; **j**·K, 865-33-8; **k**·K, 151-50-8; **l**·K, 28273-55-4; **m**·K, 7758-09-0; **n**·K, 26652-46-0; **o**·K, 19294-29-2; **p**·K, 127-08-2; **q**·K, 10387-40-3; **r**·K, 865-47-4; **s**·K, 10577-48-7; **t**·K, 3111-52-2; **u**·K, 40645-42-9; **v**·K, 71367-29-8; **w**·K, 31367-69-8; **x**·K, 40973-72-6; **y**·K, 100-67-4; **z**·K, 1122-93-6; *p*-$MeC_6H_4SO_2H{\cdot}Na$, 824-79-3; EtOH·K, 917-58-8; KOH, 1310-58-3; $Ph_2C(OMe)_2$, 2235-01-0; *p*-$PhSO_2C_6H_4COPh$, 54687-39-7; *p*-(*p*-$MeC_6H_4SO_2)C_6H_4COPh$, 97807-46-0; benzophenone, 32488-48-5; 1-nitro-1-(phenylsulfinyl)-2,2-diphenylethylene, 97825-40-6; 1-nitro-1-(phenylsulfonyl)-2,2-diphenylethylene, 97807-47-1.

Some [2 + 2] and [3 + 2] Photocycloadditions of α,β-Acetylenic Ketones

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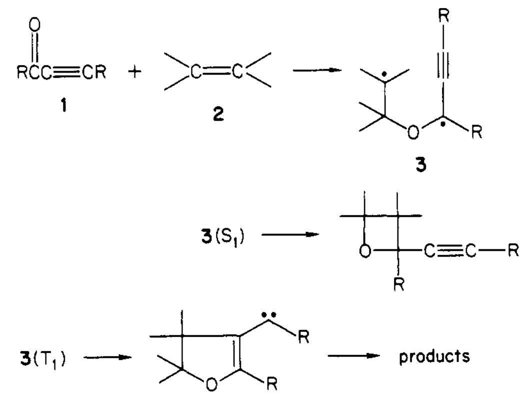
Photocycloaddition between 4,4-dimethyl-1-phenyl-2-pentyn-1-one (**7**) and the alkoxyalkenes **8** and **13** occurs in both the [2 + 2] and [3 + 2] fashions. Studies on the reaction of **7** and **13** indicate that formation of both types of product is quenched at the same rate by naphthalene and that these processes follow Stern–Volmer kinetics with $k_q\tau \sim 9.2$ M^{-1}. With 3-pentyn-2-one (**6**), **8** gives only [2 + 2] product **17**. Ketone **7** reacts with 2-butyne to yield the [3 + 2] adduct **18** and with 1,1-dimethylallene (**20**) to yield the [2 + 2] adducts **21** and **22**. These results may be contrasted with the earlier observation that triplets of ketones **6** and **7** yield essentially only [3 + 2] products from simple alkenes.

Previous studies have revealed that photochemical cycloaddition between α,β-acetylenic ketones (**1**) and simple olefins (**2**) proceeds along two paths.[3,4] The 1,4-biradical (**3**) formed from the ketone singlet and olefin closes to an oxetane (**4**), but **3** from the ketone triplet and olefin cyclizes in the [3 + 2] fashion to a vinyl carbene (**5**). Products are then formed by way of various well-precedented processes that depend on the specific substituents in **5**.[3-5] These earlier investigations concerned reactions of 3-pentyn-2-one (**6**), related alkynones, and 4,4-dimethyl-1-phenyl-2-pentyn-1-one (**7**) with simple alkenes such as tetramethylethylene, isobutylene, and 2-butene. In the present work our purpose was to examine these cyclo-



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