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Additions of Dibenzyl Selenoxides and Selenonium Ylides to an Electron-Deficient Ethylene and Acetylene

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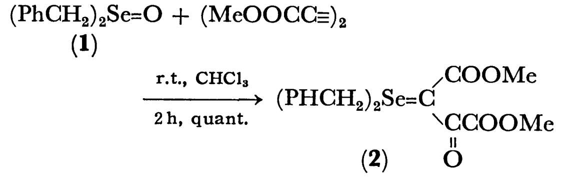
Synopsis. Dibenzyl selenoxides reacted with dimethyl acetylenedicarboxylate and tetracyanoethylene to give new ylides, while the reaction of selenonium ylides produced new ylides or cyclopropane derivatives.

Although the reactions of selenoxides and selenomium ylides have attracted attention over the last few years,[1)] no systematic study seems to have appeared on their reactions with unsaturated C–C bonds. We wish to report on the reactions obtained by use of dimethyl acetylenedicarboxylate and tetracyanoethylene (TCNE) representing an electron-deficient olefin and acetylene, respectively.

Results and Discussion

A number of addition reactions to dimethyl acetylenedicarboxylate affording ylides, known as the reverse Wittig reactions, were reported with regard to various oxides such as amine and arsine oxides,[2),3)] and sulfoxides.[4)] We have observed new examples of such reaction type, giving new ylides.

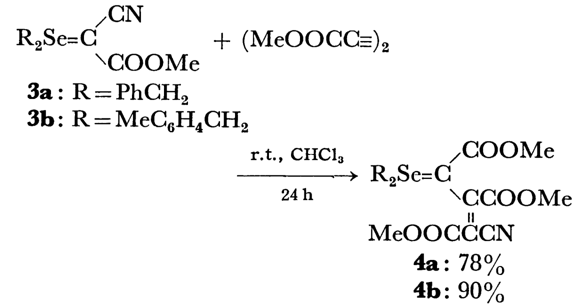
The reaction of dibenzyl selenoxide (**1**) with the carboxylate ester was found to produce the corresponding stable ylide (**2**) in a good yield.[5)] The structure of the product was easily assigned on the basis of some spectral evidence and by the independent synthesis from the correspoding selenoxide and the active methylene compound.[6)]



$$\underset{(\mathbf{1})}{(PhCH_2)_2Se{=}O} + (MeOOCC{\equiv})_2 \xrightarrow[\text{2 h, quant.}]{\text{r.t., CHCl}_3} \underset{(\mathbf{2})}{(PHCH_2)_2Se{=}C}\begin{array}{l} \diagup COOMe \\ \diagdown \underset{\underset{O}{\|}}{C}COOMe \end{array}$$

$$(PhCH_2)_2Se{=}O + MeOOCCH_2COCOOMe \xrightarrow[\text{5 min}]{\text{r.t., CHCl}_3} \mathbf{2}$$

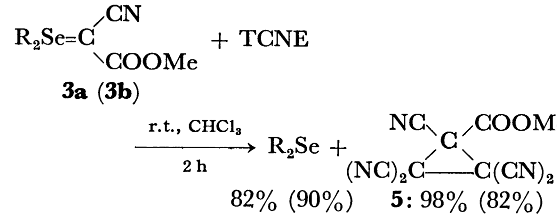
Similarly, dibenzylselenonium cyano(methoxycarbonyl)methylides, **3a** and **3b**, were allowed to react with the carboxylate at room temperature in $CHCl_3$ to afford the unstable oily ylides, **4a** and **4b**, respectively. The NMR spectrum of **4a** in $CDCl_3$ shows a multiplet between 3 and 4 ppm due to the three methoxycarbonyl methyl groups and a quartet centered at 4.2 ppm due to the benzyl protons characteristic of the dibenzylselenonium ylide, its IR spectrum displaying moderately intense bands at 2200, 1655, and 1720 cm^{-1} due to the C≡N and C=O's, respectively.



$$R_2Se{=}C\begin{array}{l} \diagup CN \\ \diagdown COOMe \end{array} + (MeOOCC{\equiv})_2 \xrightarrow[\text{24 h}]{\text{r.t., CHCl}_3} R_2Se{=}C\begin{array}{l} \diagup COOMe \\ \diagdown CCOOMe \\ \quad \| \\ MeOOCCCN \end{array}$$

3a: R = $PhCH_2$
3b: R = $MeC_6H_4CH_2$
4a: 78%
4b: 90%

A suspension of TCNE in a $CHCl_3$ solution of **3a** at room temperature immediately afforded a violet-colored solution. On being stirred vigorously for 1 h, the cyclopropane derivative (**5**) was obtained as a precipitate in an excellent yield.



3a (**3b**)

82% (90%) **5**: 98% (82%)

Trost reported on a similar decomposition reaction of dimethylsulfonium ylides in the presence of olefins to yield cyclopropane derivatives.[7)] The results can thus be explained in terms of initial addition of the starting ylide to the olefinic carbon atom to form the zwitter-ion intermediate, with subsequent three-membered ring closure on the ylide carbon to give the products.

The treatment of dibenzyl selenoxide with an equivalent of TCNE at room temperature in polar aprotic solvents such as CH_3CN and THF afforded the precipitation of dibenzylselenonium dicyanomethylide (**6**). Yields greater than 14% were not attained.

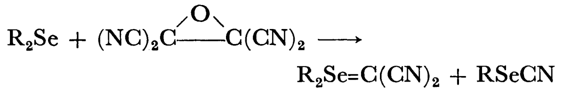
(*Reaction A*)

$$R_2Se{=}O + TCNE \xrightarrow[\text{30 min}]{\text{r.t.,}} \underset{(\mathbf{6})}{R_2Se{=}C(CN)_2} + \underset{(\mathbf{7})}{RSeCN} + R_2Se$$

1a: $PhCH_2$
1b: $MeC_6H_4CH_2$

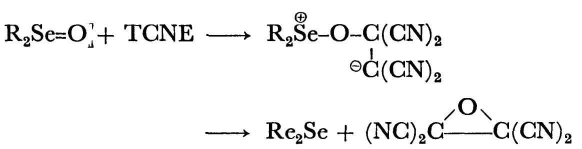
From the reaction mixture two additional products were isolated and identified as selenocyanates (**7**) and selenides. The results are summarized in Table 1 together with those for reaction B of the selenides with TCNE oxide (Table 2).[8)]

(*Reaction B*)



$$R_2Se + (NC)_2C\overset{O}{\text{——}}C(CN)_2 \longrightarrow R_2Se{=}C(CN)_2 + RSeCN$$

Several pathways to these products are possible. One of them is the formation of a selenide and TCNE oxide at the initial stage.



$$R_2Se{=}O + TCNE \longrightarrow R_2\overset{\oplus}{S}e\text{-}O\text{-}\underset{{}^{\ominus}C(CN)_2}{C}(CN)_2 \longrightarrow Re_2Se + (NC)_2C\overset{O}{\text{——}}C(CN)_2$$

The mechanism bringing about such a cyclization has been found in the reaction of ylides affording cyclopropane derivatives, referred to above. However, this pathway is highly unlikely and, even if operative, would be a minor one. The two related reactions A, and B, give the same products having markedly different ratios in the distribution of ylides and selenocyanates especially in non-polar solvents such as benzene and $CHCl_3$. The ylide formation is nil in the reaction of a selenoxide with TCNE, while it exceeds 50% in that of selenides with TCNE oxide, the yields of the selenocyanates being far higher in the latter in all solvents employed.

The results can only be rationalized by the assumption that the reaction proceeds *via* at least two common intermediates which are not so rapidly equilibrated as to give an identical product distribution for the two reactions.

Table 1. Reaction (A) of dibenzyl selenoxides with TCNE at room temperature

Selenoxide (R)	Solvent	Yield, isolated %		
		$R_2Se{=}C(CN)_2$	RSeCN	R_2Se
$MeC_6H_4CH_2$	Benzene	0	56	0
$MeC_6H_4CH_2$	$CHCl_3$	0	87	3
$MeC_6H_4CH_2$	THF	14	57	17
$MeC_6H_4CH_2$	CH_3CN	5	64	18
$PhCH_2$	THF	14	52	11
$PhCH_2$	CH_3CN	6	56	14

Table 2. Reaction (B) of dibenzyl selenides with TCNE oxide at room temperature

Selenide (R)	Solvent	Yield, isolated %		
		$R_2Se{=}C(CN)_2$	RSeCN	R_2Se
$MeC_6H_4CH_2$	Benzene	52	trace	16
$MeC_6H_4CH_2$	$CHCl_3$	65	9	4
$PhCH_2$	THF	14	15	44
$PhCH_2$	CH_3CN	10	11	43

Experimental

All the reactions were performed at room temperature in the mole ratios of 1: 1. Products except **5** and **6** were isolated by preparative TLC using $CHCl_3$ as eluant. Physical properties of products are as follows.

2: IR(KBr) 1725 (C=O), 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ=4.10 (s, 3H), 4.60 (s, 3H), 5.64 (q, 4H), 8.74 ppm (s, 10H).

4a: IR (neat) 1720 (C=O), 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ=3.78—3.93 (m, 9H), 4.87 (q. 4H), 7.44 ppm (s, 10H).

4b: IR (neat) 1725 (C=O), 1660 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.29 (s, 6H), 3.62—3.78 (m, 9H), 4.66 (q, 4H), 7.10 (s, 9H).

5: IR (KBr) 2200 (C≡N), 1775 (C=O), 1280 cm^{-1} (C–O); Found: C, 53.21; H, 1.99; N, 29.84%; M^+, 225. Calcd for $C_{10}H_3N_5O_2$: C, 53.34; H, 1.34; N, 31.10%; mol wt, 225. Mp 175—177 °C.

7a: Found: C, 48.78; H, 3.64; N, 7.17%.

7b: IR (neat) 2145 cm^{-1} (C≡N); NMR ($CDCl_3$) δ= 2.32 (s, 6H), 4.26 (s, 4H), 7.25 ppm (s, 8H); Found: C, 51.28; H, 4.22; N, 6.60%. Calcd for C_9H_9NSe: C, 51.43; H, 4.28; N, 6.67%. Mp 53—55 °C.

References

1) S. Tamagaki and I. Hatanaka, *Chem. Lett.*, **1976**, 301; S. Tamagaki, I. Hatanaka, and K. Tamura, *ibid.*, 81 (1976); S. Tamagaki and I. Hatanaka, *ibid.*, 1303 (1976).

2) H. Seidl, R. Huisgen, and R. Knorr, *Chem. Ber.*, **102**, 904 (1969).

3) E. Ciganek, *J. Org. Chem.*, **35**, 1725 (1970).

4) E. Winterfield, *Chem. Ber.*, **95**, 1581 (1965).

5) The reaction of 3,3'-dimethyl dihydrobenzoselenophene oxide with dimethyl acetylenedicarboxylate has recently been reported: H. J. Reich and J. E. Trend, *J. Org. Chem.*, **41**, 2503 (1976).

7) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 138 (1967).

8) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965).