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PHENACYLIDENEDIMETHYLSULFURANE (1)

A. William Johnson and Ronald T. Amel
Division of Natural Sciences, University of Saskatchewan
Regina Campus, Regina, Canada

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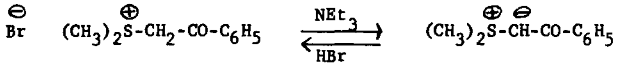
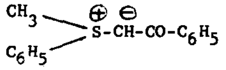
This communication concerns the preparation, isolation and study of the properties of a stable sulfonium ylid, phenacylidenedimethylsulfurane (II).

Phenacyldimethylsulfonium bromide(I), m.p. 151-152°, ν_{co} 1680 cm^{-1}, NMR spectrum in $(CD_3)_2SO$ showing a methyl singlet at 3.05 ppm(wt. 6), a methylene singlet at 5.74 ppm(wt. 2), an aromatic multiplet at 7.6-8.2 ppm(wt. 5.1) and a trace of methyl sulfide absorbing at 2.05 ppm (2), was dissolved in 95% ethanol and treated with two equivalents of triethylamine at 5-10°. Quenching with water and extraction with chloroform afforded II in 80% yield, m.p. 57-58°, ν_{co} 1508 cm^{-1} (Calcd. for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79. Found: C, 65.85; H, 6.64; S, 18.23). The NMR spectrum in $(CD_3)_2SO$ showed a methyl singlet at 2.82 ppm(wt. 6.1), a methinyl singlet at 4.43 ppm(wt. 1) and an aromatic multiplet at 7.2-8.0 ppm(wt. 5). The ylid was reconverted to its hydrobromide(I) or hydrochloride(IV), m.p. 131-132°, by treatment with aqueous hydrobromic or hydrochloric acid. The ylid appeared to be stable in the atmosphere but was hygroscopic.



$$\overset{\ominus}{Br}\quad (CH_3)_2\overset{\oplus}{S}\text{-}CH_2\text{-}CO\text{-}C_6H_5 \xrightleftharpoons[HBr]{NEt_3} (CH_3)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}H\text{-}CO\text{-}C_6H_5$$

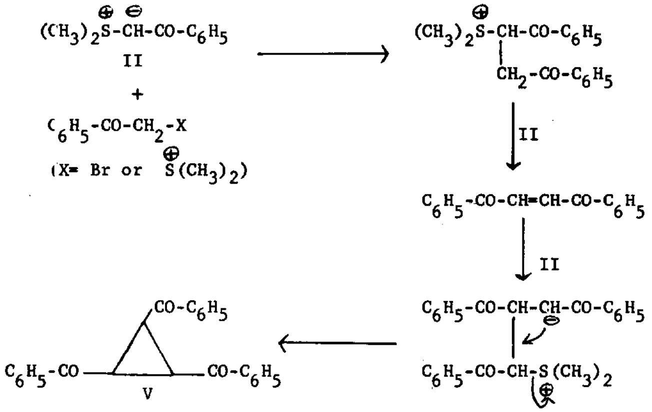
I II



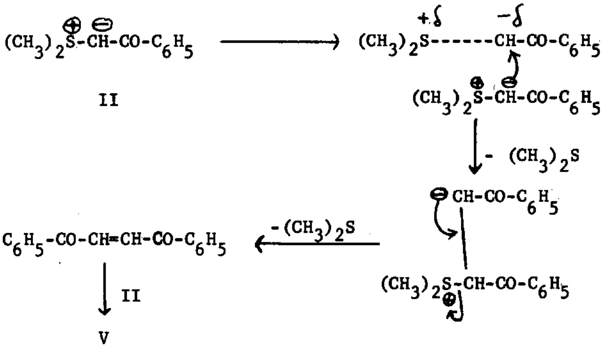
III

The characteristics of II are similar to those reported recently by Nozaki *et al.*(3) for phenacylidenemethylphenylsulfurane(III). Krollpfeiffer and Hartmann (2b) earlier had reported that the hydrobromide of III was converted into 1,2,3-tribenzoylcyclopropane(V) in the presence of aqueous sodium hydroxide. They accounted for this observation by proposing the formation of an "imaginary ylid(III)" and its decomposition into benzoylcarbene. Nozaki et al.(3) isolated III but found it to be stable to thermal decomposition and thereby claimed disproval of the benzoylcarbene hypothesis.

In accord with an alkylation-elimination mechanism(4) we have found that the sulfurane(II) reacted with the sulfonium salt(I) to afford V in 93% yield. Similarly, II and phenacyl bromide also afforded V in 94% yield. These reactions probably proceeded as follows:



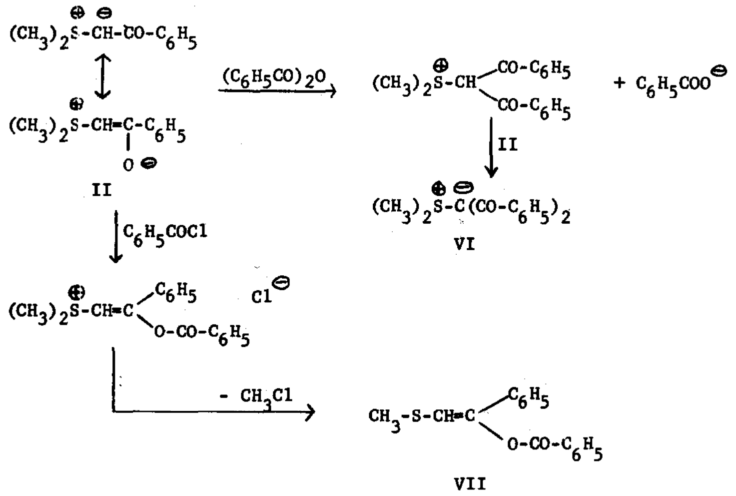
We have found, however, that II could be subjected to thermal decomposition, affording V but in low yield. Refluxing 2.5 mmoles of II for 24 hours in tetrahydrofuran afforded 1.6 mmoles of unchanged II and 0.14 mmoles (47%) of V, m.p. $218.5\text{-}219.5^{\circ}$ (Calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.50; H, 5.55). The formation of V could not have proceeded via an alkylation-elimination mechanism since the ylid(II) was shown to be uncontaminated by sulfonium salt(I) or phenacyl bromide using microanalysis and NMR spectroscopy. We suggest that a carbenoid decomposition did take place, allowing formation of dibenzoylethylene which then underwent an addition-elimination to afford V as indicated in the following mechanism:



We have studied the acylation of II. Treatment of II with an equimolar amount of benzoic anhydride in tetrahydrofuran for 43 hours at room temperature afforded a 24% yield of a new ylid, dibenzoylmethylenedimethylsulfurane (VI), m.p. 211-212°, ν_{co} 1582 cm^{-1} (Calcd. for $C_{17}H_{16}O_2S$: C, 71.84; H, 5.63; S, 11.28. Found: C, 71.17; H, 6.18; S, 11.20). The NMR spectrum in $CDCl_3$ showed a methyl singlet at 3.07 ppm(wt.6) and an aromatic multiplet at 6.9-7.5 ppm(wt. 10.5). The ylid(VI) was inert to basic hydrolysis but in dilute hydrochloric acid was cleaved to benzoic acid (55%) and phenacyldimethylsulfonium chloride(39%), both identified by melting point and infrared spectral comparison with authentic samples.

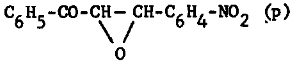
Acylation of II with an equimolar amount of benzoyl chloride in tetrahydrofuran for 22 hours at room temperature afforded a 75% yield of an enol ester(VII), m.p. 75-76°, ν_{co} 1735 cm^{-1}(Calcd. for $C_{16}H_{14}O_2S$: C, 71.12; H, 5.18; S, 11.86. Found: C, 71.09; H, 5.02; S, 11.56). The NMR spectrum in $CDCl_3$ showed a methyl singlet at 2.31 ppm(wt.3), a vinylic singlet at 6.47 ppm(wt. 1) and an aromatic multiplet at 7.2-8.3 ppm(wt. 10). The enol ester absorbed bromine and decolorized permanganate. Treatment with 50% hydrogen peroxide in acetic acid oxidized the sulfide group and cleaved the enol ester affording benzoic acid and methylphenacyl sulfone (VIII), m.p. 105-106° (Lit. (5) m.p. 106-107°), ν_{co} 1680 cm^{-1} and ν_{SO_2} 1302 and 1119 cm^{-1}.

The following mechanisms account for the observed products:



The dependence of the course of the acylation reaction on the nature of the acylating agent strikes a familiar note since Krohnke et al.(6) with pyridinium phenacylides and Chopard et al.(7) with phosphonium phenacylides both found that anhydrides resulted in C-acylation and acid chlorides resulted in O-acylation. Carroll and O'Sullivan(8) have just reported that methylphenacyl sulfone (VIII) also underwent O-acylation with benzoyl chloride.

Nozaki et al.(3) reported that III would not react with p-nitrobenzaldehyde although we had shown earlier that stable sulfonium ylids would react with benzaldehydes to afford oxiranes(9). We have now found that II reacted with p-nitrobenzaldehyde in refluxing tetrahydrofuran to afford the oxirane(IX) but only in 10% yield, m.p. 149.5-150.5° (Lit. (10), m.p. 150°), ν_{CO} 1675 cm^{-1}. The NMR spectrum in $CDCl_3$ showed two doublets at 4.28 and 4.34 ppm(wt. 2) and an aromatic multiplet at 7.3-8.4 ppm(wt. 9). A small amount of V was formed in this reaction.



$C_6H_5\text{-CO-}\underset{\setminus O /}{CH-CH}\text{-}C_6H_4\text{-}NO_2$ (p)

IX

We conclude that II is a normal but stabilized sulfonium ylid, exhibiting the properties of ylids in general and sulfonium ylids in particular. The role of the phenacyl group in stabilizing the ylid carbanion is clearly evidenced by the low wavelength of the carbonyl absorption and the ambident nature of the anion in acylation reactions.

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