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THE REACTIVITY OF DIAZO KETONES V. THE FORMATION OF 3,4,5-TRIPHENYL PYRAZOLE BY THE REACTION OF AZIBENZIL WITH SULFUR DIOXIDE IN ETHANOL.

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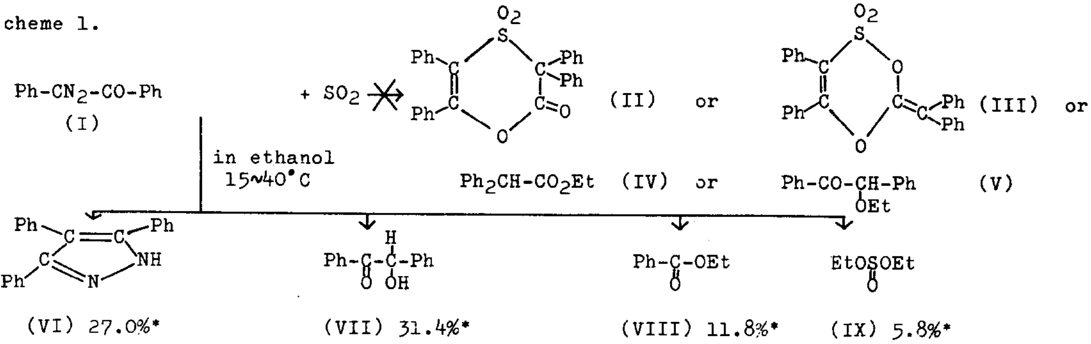
We wish to report the novel reaction of azibenzil (I) with sulfur dioxide in ethanol to give 3,4,5-triphenyl pyrazole (VI) together with benzoin (VII), ethyl benzoate (VIII) and diethyl sulfite (IX), instead of the compounds[1,2] (II, III, IV or V) (Scheme 1).

Scheme 1.



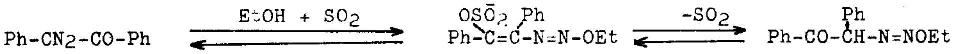
* The yields are in mole % based on I used for VII, VIII and IX, and based on a half mole of I used for VI.

The reaction of I with SO_2 gas in ethanol occurred readily at much lower temperature than the decomposition point (78°) of I, which is clearly different from the thermolysis[1] in benzene. When SO_2 gas (50g) was passed through the solution of (I) (5g) in ethanol (50ml), the temperature went up to 40° from a room temperature. The color of the solution changed from orange to yellow gradually within an hour. The reaction mixture were distillated at 40° under a reduced pressure. From the residue, white crystals of VII were obtained by adding ether. Evapolation of ether gave VI. The distilates from reaction mixtures were analyzed by a preparative gas chromatograpy, VIII and IX being confirmed.

The identification of these four products (VI~IX) was made by comparison of their infrared spectra or gas chromatographic retention times with those of the authentic samples[3,4,5,6] or mixed m.p. methods.

As described above, the reaction of I with SO_2 in ethanol proceeded at relatively low temperature to give the different results from those of photochemical or thermal reactions in benzene and n-heptane. Therefore, it seems to be difficult to explain this reaction by a carbene mechanism[1,2]. It has been reported[7] that the interaction of alcohol with sulfur dioxide givesa very small amount of $ROSO_2H$. However, the formation of $ROSO_2H$ seems not to be concerned with the present reaction, for HA type acids react[8] with diazo ketones (R_1-CN_2-CO-R_2) to yield the products, $R_1CAHCOR_2$ and R_1R_2CHCAO. Considering of these facts it may be suggested that the stabilized species[9] are concerned with the initial step of the present reaction (Scheme 2).

Scheme 2.



$$Ph\text{-}CN_2\text{-}CO\text{-}Ph \xrightleftharpoons{EtOH\ +\ SO_2} Ph\text{-}\overset{O\bar{S}O_2}{C}{=}\overset{Ph}{C}\text{-}N{=}N\text{-}OEt \xrightleftharpoons{-SO_2} Ph\text{-}CO\text{-}\overset{Ph}{C}H\text{-}N{=}NOEt$$

At present stage, however, it is too difficult to describe the mechanism of this reaction in detail. Further work is in progress with regared to scope and limitation of this reaction.

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