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# ON SYNTHESES OF ALKYL DIAZOPROPIONATES[1]

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THE ANGUISH[3] and confusion[4] of some of our colleagues, as well as current disorder in the literature prompts us to provide the correct structure of a compound alleged to be ethyl diazopropionate (1a) and to summarize the published data on the various methods of preparation of similar compounds. Diazopropionates are of considerable synthetic potential, even though one would expect them to yield carbenes prone to give acrylates by intramolecular insertion.

As early as 1904 Curtius and Müller[5] reported the diazotization of the ethyl ester of alanine to give 1a (Path A). In 1955 Perold[6] repeated this preparation, but gave no more details on the physical properties. In 1964, White and Baumgarten[7] described the formation of 1a on pyrolysis of ethyl N-carboethoxy-N-nitrosoalanine (Path B). A year later Harvey[8] proposed a general synthesis utilizing the reaction of phosphorus ylid 2 with tosyl azide (Path C). Finally, Regitz, Menz and Rüter[9] adapted the diazo transfer reaction to the synthesis of 1a (Path D). Unhappily, the "1's" produced by these diverse methods are patently not identical. Table I summarizes the available physical data from these earlier preparations as well as from a new method, Path E. The new route involves the thermal decomposition of the tosyl hydrazone salt of the corresponding pyruvate. Path C produces a material different in physical and spectral properties from the others.

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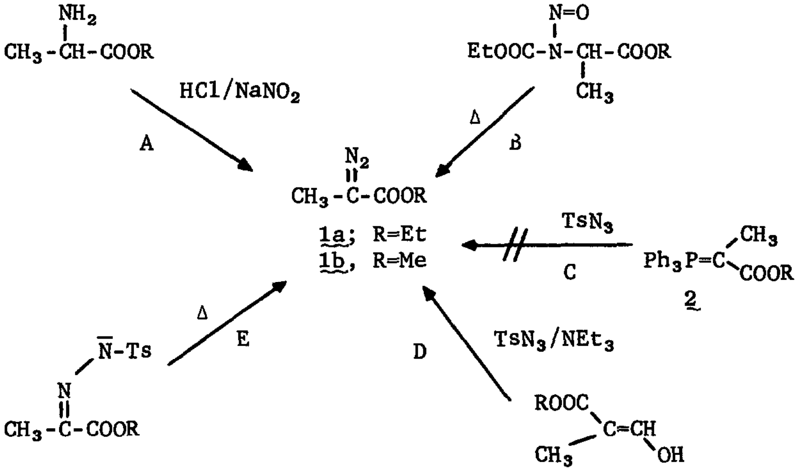


| Method | $\nu$ $C=N_2$ ($cm^{-1}$) | nmr($\delta$) | bp (mm) | $n_D$($^oC$) | color |
|---|---|---|---|---|---|
| Curtius and Müller | -- | -- | 65-8 (41) | 1.4472(18) | golden-yellow |
| (Perold) | -- | -- | -- | -- | -- |
| | " consistent" | -- | | 1.4489 | yellow |
| | 2105 | 1.3(3H),1.55(3H),<br>4.2(2H) | 50(.2) | 1.4474(24) | colorless |
| | 2083 | -- | 68 (41) | -- | -- |
| | 2082 | 1.25(3H),1.96(3H),<br>4.2(2H) | -- | -- | yellow |

Table I. Properties of 1a.

Curtius and Müller[5] had also synthesized the methyl ester 1b, but eported only a scanty description. We have repeated the preparation of 1b y routes A, C and E. Table II summarizes the data. Again Path C produces different compound. Thus the difficulty in making adducts from 1a or 1b ade by Path C is apparent. The product of the reaction is not a diazoter.

| Method | $\nu$ $C{=}N_2$ ($cm^{-1}$) | nmr ($\delta$) | bp(mm) | $n_D$(°C) | color |
|---|---|---|---|---|---|
| A (Curtius and Müller) | -- | -- | 43-5(11) | 1.4487(20) | golden yellow |
| A (This work) | 2084 | 3.74(3H),1.98(3H) | 52(18) | --- | yellow |
| C (This work) | 2110 | 3.72(3H),1.55(3H) | 44(.2) | --- | colorless |
| E (This work) | 2084 | 3.74(3H),1.98(3H) | -- | --- | yellow |

Table II. Properties of 1b.

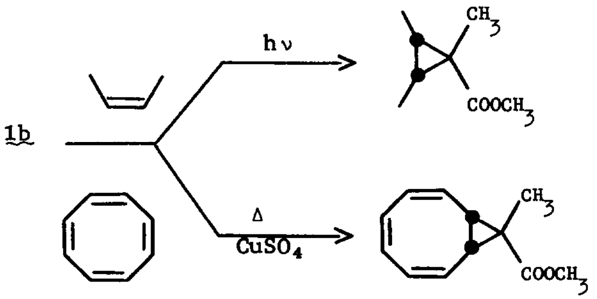
Although the differences in infrared and nmr spectra do not permit a determination as to which compound is the diazopropionate, the differences in color and boiling point make it unlikely that the product of Path C can be identical or even isomeric with 1a or 1b. Our initial guess as to the correct structure of the product of Path C was the bis-azide 3. Fortunately 3 could be made by an adaptation of the method of Moriarty.[10,11] It proved in all respects to be identical to " 1a" and " 1b" made by Path C.

$$CH_3\text{-}CBr_2\text{-}COOR \xrightarrow{NaN_3} CH_3\text{-}\overset{N_3}{\underset{N_3}{C}}\text{-}COOR$$

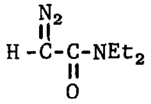
3a; R = Et

3b; R = Me

Elemental analysis further confirmed the assignment. Finally, it is worth noting that Paths A, D and E (and doubtless B) give a material which does form adducts to olefins on thermal,[6] photolytic[12] or copper-catalyzed decomposition.



In the paper reporting Path C[8] the syntheses of ethyl diazoacetate and the diazoamide **4** by analogous routes were claimed. Path C does indeed yield ethyl diazoacetate, but not **4**.[13] The role of the alkyl group in changing the product from the diazocompound to the bis-azide is yet to be clarified.



$$H-\overset{\overset{N_2}{\|}}{C}-\underset{\underset{O}{\|}}{C}-NEt_2$$

**4**

## REFERENCES AND NOTES

1. Support of this work by the National Science Foundation through Grant GP-12759 is acknowledged with appreciation.

2. National Science Foundation Predoctoral Fellow, 1967-71.

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11. R. M. Moriarty and P. Serridge, *ibid.*, **93**, 1535 (1971). We thank Professor Moriarty for helpful advice on the synthesis.

12. This part of the work is taken from the Ph.D. Thesis of R. R. Rando, Yale University, New Haven, Connecticut, 1967.

13. For the correct physical properties of **4** see R. R. Rando, *J.Amer.Chem.Soc.*, **92**, 6706 (1970).