Pak. j. sci. ind. res., vol. 32, no. 3, March 1989

THE REACTIONS OF ETHYLACETODIAZOACETATE AND DIMETHYLDIAZOMALONATE WITH CYLOHEPTENE IN THE PRESENCE OF COPPER (II) ACETYLACETONATE

Olcay Anac, Tülay Mazlumoğlu and A. Cevdet Aydoğan

Department of Chemistry, Faculty of Science, Technical University of Istanbul, Turkey

(Received January 14, 1989)

New compounds were obtained from a catalysed reaction of ethylacetodiazoacetate (eada) with cycloheptene. Reactivities of eada and dimethyldiazomalonate (dmdm) were compared by investigating the reaction of a mixture of these two diazocompounds with cycloheptene. The dimers and crossed dimers were also synthesized separately and used in the analysis of the reaction products. Dmdm was found to be more reactive and more electrophilic.

Key words: Ethylacetodiazoacetate, Cycloheptene, Dimethyldiazomalonate.

INTRODUCTION

Carbene and carbenoids are highly reactive intermediates which undergo addition, insertion and dimerization reactions with olefins, depending on reaction conditions. [1-10] Carbenes and carbenoids derived from ∝-diazocarbonyl compounds are neutral but have electrophilic character. They have medium selectivity because of their mesomeric stability. It is generally recognized that singlet and triplet carbenes are formed by direct or sensitized irradiation. Although several mechanistic and synthetic approaches have been proposed for the metal-salt catalysed reactions of carbenes, there is still not a distinct explanation. Some approaches are based on a carbenoid intermediate, a carbene-catalyst complex.

Insertion of carbenoids into C-H bonds which have the most weakly bound and the least hindered hydrogen occurs to a small extent. The insertion may take place through a direct, a zwitter-ionic or a radical mechanism. Dimerization of carbenes may take place i) by combination of two carbenes or ii) by combination of two radicals formed from the decomposition of diazo compounds. In the carbene/carbenoid reactions, the main products are generally addition compounds. The electrophilicity of carbenes towards double bonds is an important factor in these reactions.

EXPERIMENTAL

Spectroscopic and gas chromatographic studies. Infrared spectra were measured on a Schimadzu IR-400 model spectrophotometer and ^{1}H-NMR on a Bruker 200 MHz model instrument using TMS as an internal standard. Gas chromatographic studies were performed on a Schimadzu instrument, model 5A, equipped with F.I.D. detector. OV-17, 3% on chromosorb w 100/120 mesh, 3 mm I.D. x 3 m (I) and carbowax 20-M 25% on Shimalite 60/80 mesh, 3 mm I.D. x 3 m (II) columns were used. The following conditions were imposed. Injector and detector temperature 200°, carrier gas (N_2), 100 ml/min, temperature programme 105-295° at 5°/min, isothermal at 170° for II. Integrator, ITG-4A. Reproducibility of results was ± 0.5% under the same conditions. Internal standards were used for calculation. Three runs were carried out in each case. Elemental analyses were performed on a Hereaeus microstandard equipment.

Preparative thin-layer chromatography studies. PTLC studies were carried out using silicagel HF_{254} layers (1 mm) and CH_2C1_2:$CC1_4$ *n*-hexane, ethylacetate (75:10:10:5) and solvent. As detection spray (for pattern plate only), 3.5% ethanolic solution of phosphomolybdic acid is used. The plate is heated to 160° for 30 mins. The sample was applied on to the plate by DESEGA microdoser equipment.

Preparations of starting materials and standards. In our previous papers, we had synthesized some of compounds related to this study *p*-toluene sulphonylazide was prepared by the method of Baumgarten. [16] Yield was 91% (higher than the literature value [12-14] dimethyldiazomalonate (from *p*-toluene sulphonylazide), tetramethoxy-carbonylethane (7), tetramethoxycarbonylethylene (6) and 8, 8-dimethoxycarbonylbicyclo (5.1.0) octane (5) were prepared by the method of Wulfman and co-workers [10, 12-14]. In this work we also synthesized the compounds shown below, ethylacetodiazoacetate having 99.5% purity (from *p*-toluene sulphonylazide) was prepared by the method of Regitz [17]. IR, UV, elemental analysis data were in accordance with Regitz's. ^{1}H-NMR (δ) ($CDC1_3$): 1.34 (t-3H, J:7c/s, methyl), 2.48 (s-3H, ketonic methyl), 4.31 (q-2H, 7 and 7 c/s, CH_2).

Diacetyl-di-ethoxycarbonylethane (3) and diacetyldiethoxycarbonyl-ethylene (4) standards were prepared by similar procedures noted above starting with ethylacetodiazoacetate and ethylacetoacetate for 3 and only ethylacetodiazoacetate for 4 in benzene having copper (II) acetylacetonate as catalyst.

(3) IR (cm^{-1}): 2950 (vs C-H), 1720 (vs C = 0). ^{1}H-NMR

(δ) (CDC1$_3$) 1.3 (t-3H,7 c/s, methyl), 2.4 (s-3H, ketonic methyl), 3.84 (s-2H, acetonyl p.), 4.23 (q-2H, J:7 c/s, 7 c/s, CH$_2$). Anal. calcd. for $C_{12}H_{18}0_6$: C, 55.81: H, 7.03; found C, 55.92; H, 7.20%.

(4) *Cis*-dimer could not be formed because of steric hindrence. IR (cm^{-1}): 2945 (vs C-H), 1720 (vs C = O). ^{1}H-NMR (δ) (CDC1$_3$): 1.34 (t-3H, J: 7c/s, methyl), 2.45 (s-3H, ketonic methyl), 4.11 (q-2H, J: 7 and 7 c/s CH$_2$). Anal. calcd. for $C_{12}H_{16}O_6$: C, 56.24; H, 6.29; found C, 56.18; H, 6.37%.

The standards for the probable crossed-dimers; l-acetyl, 1-ethoxycarbonyl, 2, 2-dimethoxycarbonylethane (8) and l-acetyl, 1-ethoxycarbonyl, 2, 2-dimethoxycarbonylethylene (9) for the comparison reaction were also synthesized by the same procedure. GC analysis of thecrude products 8 and 9 showed the presence of other possible dimers 3,7 and 4,6. The zones for 8 and 9 were extracted from PTLC and identified as shown below.

(8) IR (cm^{-1}): 2900, 2850 (vs C-H), 1740, 1720, 1618 (vs C=0). ^{1}H-NMR δ (CDC1$_3$): 1.27 (t-3H, J: 7 c/s, methyl), 2.41 (s-3H, ketonic methyl), 3.77 and 3.87 (s-3H, s-3H, methyl, methyl), 4.2 (q-2 H, J: 7 and 8 c/s, CH$_2$), 4.34 (m-2H, malonyl and acetonyl p.). Anal. calcd. for $C_{11}H_{16}O_7$: C, 50.77; H, 6.19; found C, 50.85; H, 6.21%.

(9) IR (cm^{-1}): 2900, 2850 (vs C-H), 1718, 1620 (vs C = 0). ^{1}H-NMR (δ) (CDC1$_3$) 1.32 (t-3H, J: 7 c/s, methyl), 2.3 (s-3H, ketonic methyl), 3.77 and 3.83 (s-3H, s-3Hmethyl), 4.3 (m-2H, CH$_2$). Anal. calcd. for $C_{11}H_{14}O_7$: C, 51.16; H, 5.46; found C, 51.31; H, 5.50%.

Procedure for catalyzed reaction of ethylacetodiazoacetate with cycloheptene. The amounts used Cu (AcAc)$_2$ 0.14 mmol, diazo compound 0.02 mol. A solution of catalyst in olefin (0.25 mol) was refluxed, while a solution of diazo compound in olefin (0.25 mol) was added dropwise. After completion of olefin addition sample taken from the continuing reaction at time intervals were analyzed by GLC and IR in order to ensure the end of reaction. The mixture was filtered while hot, the excess olefin was recovered by vacuum distillation. The residue was analyzed by GLC and PTLC. The main zones were extracted from PTLC and recontrolled by GLC and identified as 1 and 2.

(1) *8, 8-acetylethoxycarbonylbicyclo (5.1.0) octane.* IR (cm^{-1}): 3000, 2850, 1450 (vs C-H), 1740 (vs C = O), ^{1}H-NMR (δ) (CDC1$_3$) 1.27 (t-3H, J: 7 c/s, methyl), 1.3-2 (m-10H, ring p.), 2.45 (s-3H, ketonic methyl) 3.43 (q-1H, J: 7 and 7 c/s, bridgehead), 4.1 (m-1H, bridgehead) 4.2 (q-2H, CH$_2$). Anal. calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; found C, 69.98; H, 9.03%.

In addition to the main peaks in ^{1}H-NMR, presented above, the other sub-peaks appearing approximately at the same ranges suggested that compound was an exo-endo derivative.

(2) *Ethylaceto (3-cycloheptenyl) acetate.* IR (cm^{-1}): 3010, 2950, 1450, (vs C-H), 1650 (vs olefinic C-H), 1735 (vs C = O). ^{1}H-NMR (δ) (CDC1$_3$) 1.3-2 (m-8H, ring p.), 1.28 (t-3H, J: 7 c/s methyl), 2.45 (s-3H, ketonic methyl), 3.43 (m-1H, acetonylp.), 4.2 (q-2H, J: 7 c/s, CH$_2$), 5.65 and 5.85 (m-1H, m-1H, vinyl). Anal. calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; found: C, 69.72; H, 8.92%.

Comparison reaction of dmdm and eada with cycloheptene. Equal moles of dmdm and eada (3.2 mmol 3.2 mmol) were reacted with only 3.2 mmol of cycloheptene in the presence of excess benzene (76.8 mmol). The other reaction conditions were the same given above. Samples taken from the continuing reaction at different times were analyzed by GLC and exhaustion profile given in Fig. 1 was obtained. The mixture of products was analyzed by using the standards, which were prepared as described above.

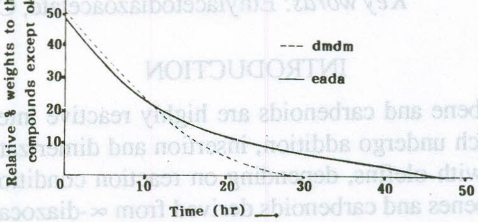
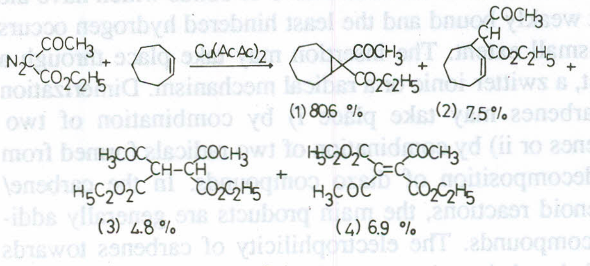


Fig. 1. Consumption of dmdm and eada versus time.

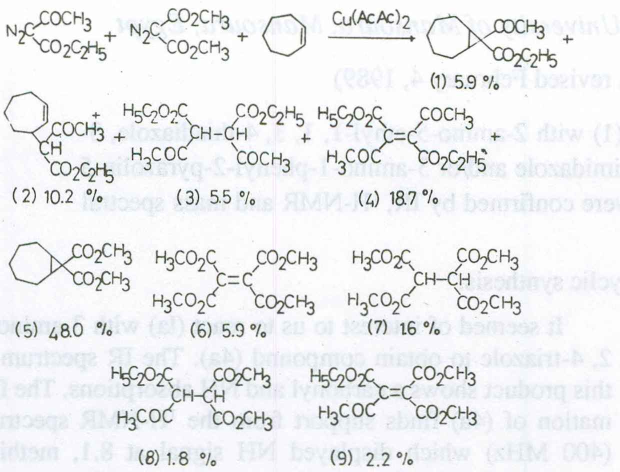
RESULTS AND DISCUSSION

In this study, eada [11], which has been used as a carbene precursor to a small extent only, was synthesized and reacted with excess cycloheptene in the presence of copper (II) acetylacetonate. The compounds (1-4) were obtained. the ratios of the weights of individual compounds to total products weight are given in Scheme 1.



Scheme 1

In our previous papers [12-14], we reported the synthesis of 8,8-di-methoxycarbonylbicyclo (5.1.0) octane (5) by the reaction of dmdm with excess cycloheptene using copper (II) acetylacektonate as catalyst. As any insertion product could not be identified in this reaction we concluded that the reaction of dmdm with cycloheptene led to cyclopropane whereas eada gave both cyclopropane and C-H insertion. The synthesis of related carbene-dimers [6, 7] by separate reactions were also reported. There are many works in which the relative reactivities of a series of olefins to the same carbene/carbenoids were studied in detail [4, 15]. Similarly, as continuation of our work on the reaction of eada and dmdm with cycloheptene, the reactivities of these compounds towards the same olefin were investigated. For this purpose, an equimolar mixture of dmdm and eada was reacted with equimolar of cycloheptene in the presence of excess benzene. The results are presented in Scheme 2.



Scheme 2.

The reactions of ethylacetodiazoacetate and dimethyldiazomalonate with cycloheptene in the presence of copper (II) acetylacetonate.

Samples taken from the reaction mixture at time intervals were subjected to glc and the data obtained is presented in the form of exhaustion profiles for both of the diazo compounds (Fig. 1).

All possible dimers [3, 4] including "crossed" dimers [8, 9] were also synthesized by suitable reactions and used as standards in the analysis of the mixture. The details of the reactions mentioned above are described in the experimental section.

As shown in (Fig. 1), the rate of reaction with dmdm is higher. In Scheme 2, the percentage of addition product of ethoxyacetylcarbenoid is less than the percentage of its insertion product. For the possibility of the solvent effect on the ratio difference between (1)/(2) in the two experiments the first one was repeated using of an equimolar mixture of eada with cycloheptene in the presence of excess benzene. Solvent effect was not so significant as revealed from the similar product distribution in both cases. Considering that the electrophilicities of carbenoids are rather influential in addition reactions, dimethoxycarbonylcarbenoid should be more electrophilic than the ethoxyacetylcarbenoid. However there is no distinct difference between structures or steric models of these carbenes. The difference may be due to inductive effects which give a higher electrophilicity to dimethoxycarbonylcarbenoid.

REFERENCES

1. M. Jones Jr. and R.A. Moss, *Carbenes* (Wiley-Interscience 1973).
2. N.S. Isaacs, *Reactive Intermediates in Organic Chemistry* (Wiley-Interscience, 1974), pp. 375.
3. M. Jones and R.A. Moss, *Reactive Intermediates*, A. Serial Publication, (Wiley-Interscience 1978), Vol.1, pp. 69.
4. W. Kirmse, *Carbene Chemistry, Organic Chemistry*, A Series of Monographs (Academic Press, 1971).
5. E. Muller and Houben-Weyl, *Methoden der Organischen Chemie* (Photochemie 4/5b, George Thieme Verlag, 1975), Vol. 2, pp. 1158.
6. D.S. Wulfman, N.V. Thinh, R.S. McDaniel and B.W. Peace, J. Chem. Soc., Dalton Trans., 522 (1975).
7. D.S. Wulfmann, Tetrahedron, 32, 1231 (1976).
8. D.S. Wulfman, R.S. McDaniel and B.W. Peace, Tetrahedron, 32, 1241 (1976).
9. D.S. Wulfman, B.W. Peace, R.S. McDaniel, Tetrahedron, 32, 1251 (1976).
10. D.S. Wulfman, B.G. McGibboney, E.K. Steffen, N.V. Thinh, R.S. McDaniel and B.W. Peace, Tetrahedron, 32, 1257 (1976).
11. M. Regitz, Chem. Ber., 99, 3128 (1966).
12. O. Anac, C.A. Aydogan, Chim. Acta Turc., 10 (2), 113 (1982).
13. O. Anac, C.A. Aydogan and Y. Yagcl, Chim. Acta Turc., 11 (2), 221 (1983).
14. O. Anac, Rev. Roum. de Chimie, 31 (8), 787 (1986).
15. V.C. Solomon and H. Kochi, J. Amer, Chem. Soc., 95 (10), 3308 (1973).
16. H.E. Baumgarten, *Organic Synthesis* (Wiley, 1973) Vol. 5, pp. 179.