PHASE TRANSFER CATALYZED C- *vs* O- ALKYLATION OF 3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONE IN THE ABSENCE OR PRESENCE OF CARBON DISULPHIDE

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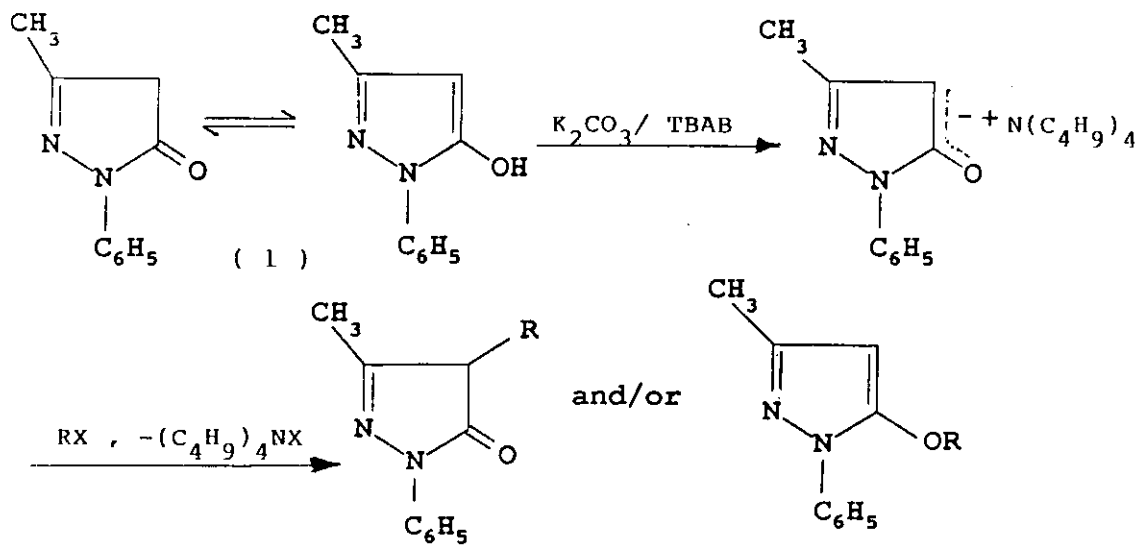
Abstract - 3-Methyl-1-phenyl-2-pyrazolin-5-one (1) was treated with different bromoorganic compounds such as benzyl bromide, 1,3-dibromo - propane,methyl bromoacetate, bromoacetaldehyde diethylacetal as alkylating agents either in the absence or in the presence of carbon disulphide and under phase - transfer catalysis conditions aimed at studying the reactivity of the title compound with respect to C- *vs* O- alkylation .

In continuation of our previous work on phase-transfer catalysis [1] and pyrazolone chemistry ,[2,3] we undertook to study the reactivity of C4- *vs* O- alkylation towards some bromoorganic compounds as alkylating agents in the absence or in the presence of carbon disulphide under phase- transfer catalysis (PTC) conditions as a versatile tool compared with the classical base - catalyzed

alkylation reactions which sometimes give low yields and complex mixtures which were less easy to separate . [4,5]

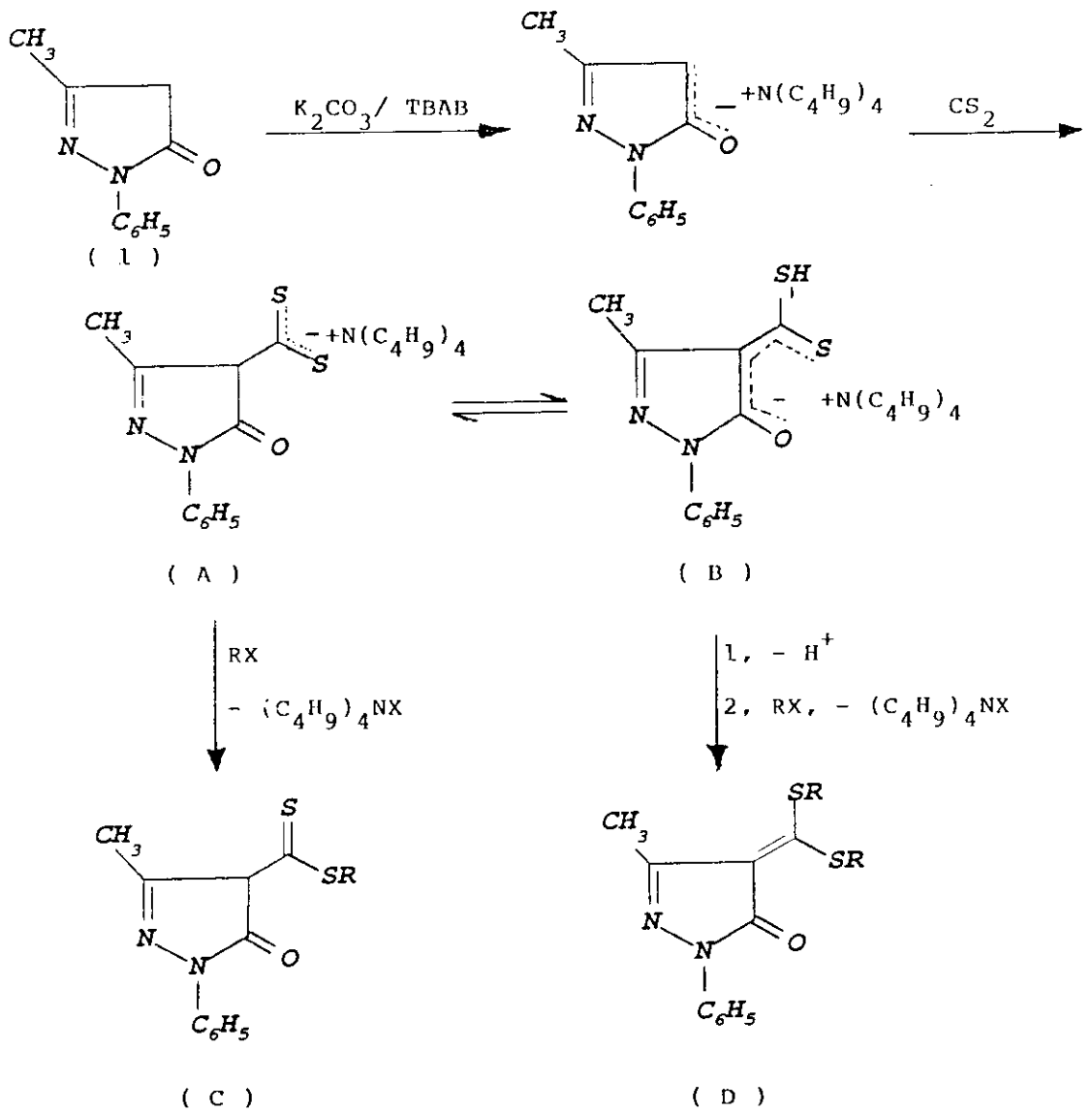
After a thorough practical investigation , we found that the optimum conditions of PTCalkylation of 3-methyl-1-phenyl-2-pyrazolin-5-one (1) is a liquid / solid phase combination using benzene as a liquid phase and anhydrous potassium carbonate as a solid phase and mild base , while tetra-butylammonium bromide (TBAB) is the catalyst . The reactions were done at 20°C (room temperature) with vigourus stirring and were completed within 18 - 48 hours depending on the nature of the alkylating agents and the absence or the presence of carbon disulphide .

Deprotonation of either the keto or the enol forms of the pyrazolone (1) may give a delocalized ambident anion in the presence of potassium carbonate as a mild base. Tetrabutylammonium ion extracts the pyrazolone anions and transfers it into the organic liquid phase which gives it high tendency to react with the alkylating agents via nucleophilic displacement .



(C - alkylation) (O - alkylation)

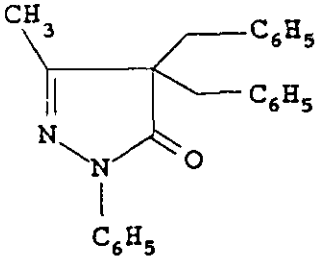
In a one pot PTC reaction of pyrazolone(1)in the presence of carbon disulphide and organic bromo compounds , the pyrazolone ambident anion underwent nucleophilic addition on carbon disulphide predominantly at C4 to give the tautomeric dithioacid anion (A) and the delocalized keto dithioacid anion (B) , respectively . The former may be monoalkylated to give the dithioester (C) , while the latter may be deprotonated and again alkylated to give a ketene dithioacetal (D) .



Many heterocyclic tautomeric systems gave mixtures of products ; [6-8] the better leaving groups of the alkylating agents are chosen , the higher is the yield of O - alkylation . Compared to the conditions applied in these cases , the ion pair extraction (PTC) is easier , safer and may be carried out at room temperature . In our hands , the reactions may be driven to preference of O - alkylation , except for benzylation with benzyl bromide (see below) .

It is known that the direction of C - *vs* heteroatom alkylation becomes more complex and it is a function of many factors such as substrate structure , alkylating agent , solvent , concentration , nature of the cation , temperature , etc ..... . [9-11]

PTC alkylation of 3-methyl-1-phenyl-2-pyrazolin-5-one (**1**) by benzyl bromide in the absence of carbon disulphie gives, after 24 hours , 4,4-dibenzyl-3-methyl-1-phenyl-2-pyrazolin-5-one (**2**) in 34 % yield , while in the presence of carbon disulphide gives, after 18 hours , 5-benzyloxy - 3-methyl-1-phenyl-1H-pyrazole (**3**) in 16 % yield and 4-(bisbenzylthio) methylene-3-methyl - 1-phenyl-2-pyrazolin-5-one (**4**) in 48 % yield .



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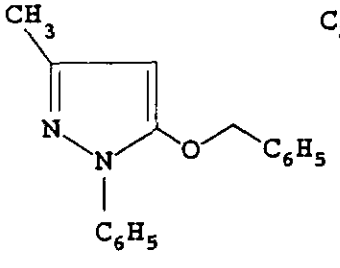

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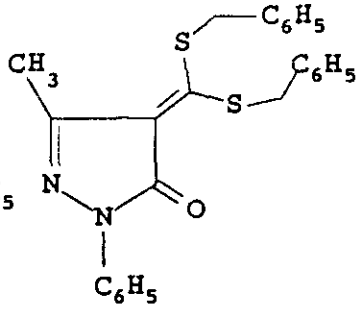
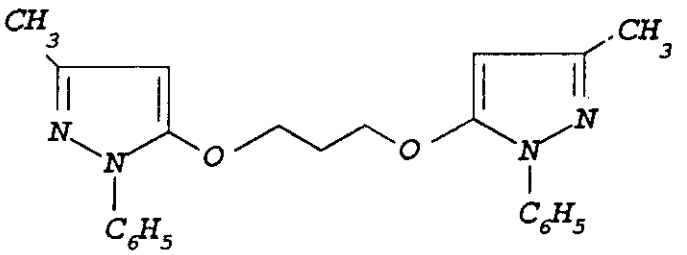


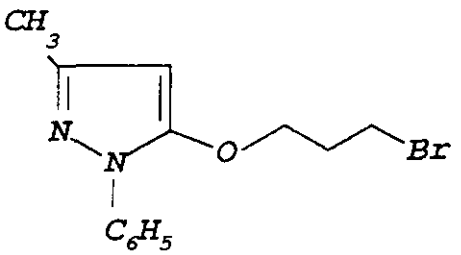
(4)

The formation of benzyloxypyrazole (**3**) may be attributed to the presence of carbon disulphide as a polar reagent , since polar solvents favour O - alkylation . [11]

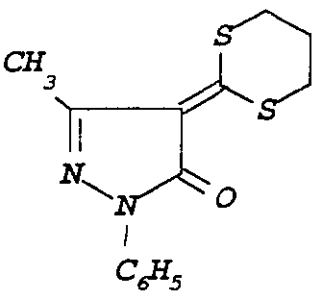
Treatment of the pyrazolone (**1**) with 1,3-dibromopropane under PTC reaction conditions in the absence of carbon disulphide gives after 48 hours , 1,3-di(3-methyl-1-phenyl-1H-pyrazol-5-yl -oxy)-propane (**5**) in 17 % yield and 1-bromo-3-(3-methyl-1-phenyl-1H-pyrazol-5-yloxy) -propane (**6**) in 46 % yield . The reaction proceeds , predomenantly *via* O - alkylation , while the reaction of pyrazolone (**1**) under PTC conditions with 1,3-dibromopropane in the presence of carbon disulphide gives **6** after 18 hours in 10 % yield and 4-(1,3-dithian-2-ylidene)-4,5-dihydro -3-methyl-5-oxo-1-phenyl-1H-pyrazole (**7**) in 62 % yield .



(**5**)



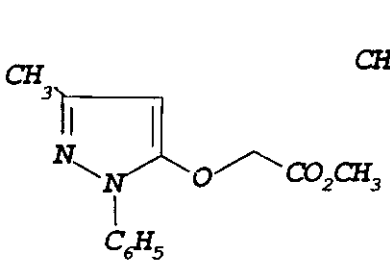
(**6**)



(**7**)

On the other hand , alkylation of pyrazolone (**1**) by methyl bromoacetate under PTC reaction conditions and the absence of carbon disulphide yields after 48 hours , methyl (3-methyl-1-phenyl-1H-pyrazol-5-yloxy) acetate (**8**) in 30 % yield and methyl [5-(methoxycarbonyl-methoxy)-3-methyl-1-phenyl-1H-pyrazol-4-yl] acetate (**9**) in 29 % yield ,while in the presence of carbon disulphide after 18 hours , **8** is obtained in 21 % yield and 4-[bis-(methoxycarbonyl-

methylthio)- methylene]-4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazole (**10**) in 53 % yield .



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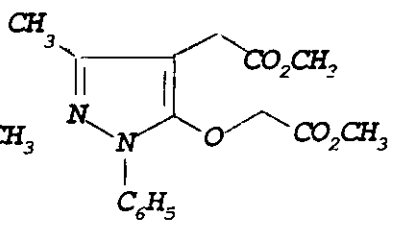

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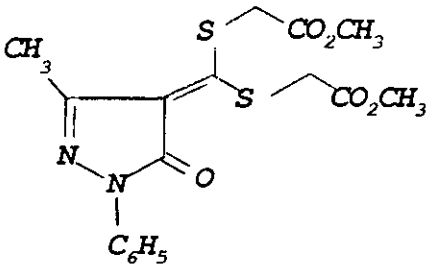
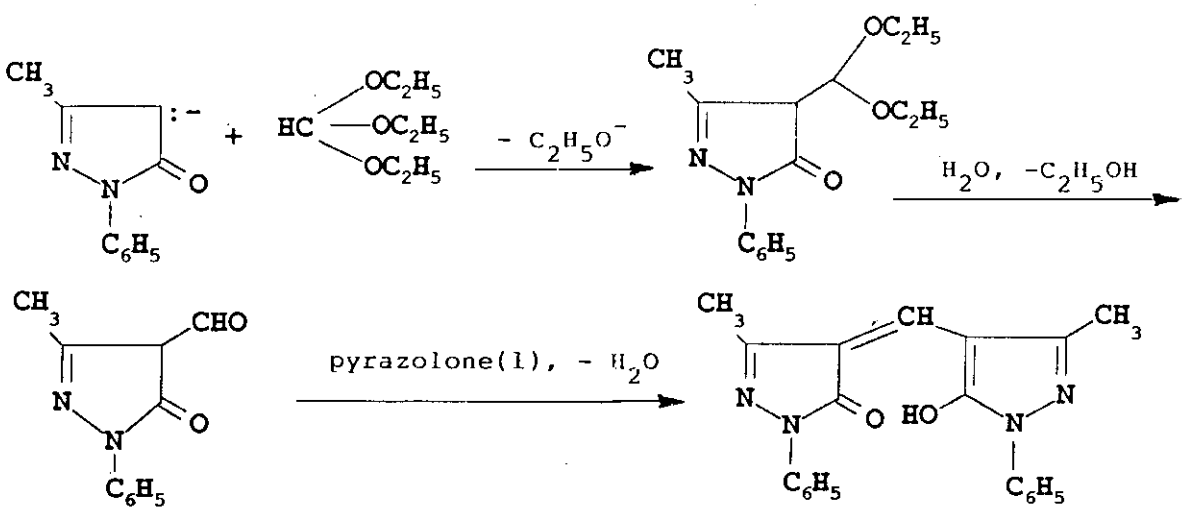


(10)

Finally , a trial of alkylation of the pyrazolone (**1**) by bromoacetaldehyde diethylacetal as sterically hindered alkylating agent with decreased S_{N2} reactivity under PTC reaction conditions in the absence of carbon disulphide gives after 48 hours , the known 4,4'-methine-bis (3-methyl-1-phenyl-2-pyrazolin-5-one) (**11**) in 25 % yield . The formation of methine-bis-pyrazolone (**11**) may be attributed to the presence of triethyl orthoformate in the commercial bromoacetal which causes formylation of pyrazolone (**1**) faster than alkylation by bromoacetal according to the following steps:

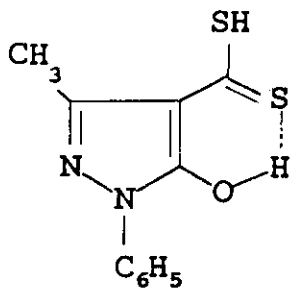


(11)

Also , the bispyrazolone (**11**) is formed in quantitative yield upon treatment of pyrazolone (**1**) with triethyl orthoformate under the same PTC reaction conditions .

Treatment of pyrazolone (**1**) with bromoacetaldehyde diethylacetal under PTC conditions and presence of carbon disulphide afforded after 36 hours , a 9 % yield of **11** and (4,5-dihydro-3-methyl -5-oxo-1-phenyl-1H- pyrazol-4-yl) dithiocarboxylic acid (**12**) in 46 % yield , which are separated by acidification of potassium carbonate solution .

Treatment of pyrazolone (**1**) with carbon disulphide in the absence of organic bromo compounds and under PTC conditions gives after 72 hours the dithiocarboxylic acid (**12**) in 78 % yield .



(12)

EXPERIMENTAL

Melting points (uncorrected): Reichert thermovar hot-stage microscope-Elemental analysis :Carlo Erba Mod 1106 CHN analyzer-IR spectra : Perkin- Elmer Spectrophotometer 983-^{1}H- and ^{13}C-NMR : Bruker DRX 500 in $CDCl_3$ using TMS as internal standard ^{13}C- signals assigned on the basis of the DEPT.135/90 spectra -Mass spectra: AMD 604 with direct inlet at 70 eV - Preparative layer chromatography (PLC): 48 cm wide and 20 cm tall glass plates covered with 1.0 mm thick layer of slurry, air-dried silica gel Merck PF_{254}- Preparative column chromatography: 50 cm tall and 5 cm diameter glass column packed with silica gel with size 0.2 - 0.5 mm and mesh 35-70 - 3-Methyl-1-phenyl-2-pyrazolin-5-one is a Merck Product.

General procedure of PTC- alkylation of 3- methyl-1- phenyl-2- pyrazolin-5-one (1):

a) In the absence of carbon disulphide : A solution of pyrazolone (1) (1.73 g, 0.01 mol), tetrabutylammomium bromide (TBAB, 0.6 g, 0.002 mol), bromo organic compound or triethyl orthoformate (0.02 mol ; except in using 1.3- dibromopropane, 0.01 mol) and anhydrous potassium carbonate (3.0 g , 0.02 mol) in dry benzene(50 mL) was kept at 20 °C with vigorous stirring.The progress of the reaction was monitored by TLC. The reaction was completed within 24-48 h and the solution was filtered off. The solid potassium carbonate residue was dissolved in water (50 mL) and acidified by 10% hydrochloric acid solution in an ice-bath which gives no precipitate in all cases. Benzene was evaporated from the organic liquid phase and the residue was subjected to PLC plates or column chromatography to separate the products using the proper eluent.

b) In the presence of carbon disulphide: A solution of pyrazolone (1) (1.73 g, 0.01 mol), tetrabutylammonium bromide (TBAB, 0.6 g, 0.002 mol) , carbon disulphide (10 mL) and anhydrous potassium carbonate (3.0 g , 0.02 mol) in dry benzene (50 mL) was kept at 20 °C with vigorous stirring for 3 h, then the bromo organic compound (generally 0.02 mol except when using 1,3- dibromopropane, 0.01 mol) was added and the vigorous stirring was continued.

The progress of the reaction was monitored by TLC which is completed within 18 - 72 h.

The solution was filtered off and the solid potassium carbonate residue was dissolved in water (50 mL) and acidified by 10 % hydrochloric acid solution in an ice-bath which gives no precipitate in all cases except in the absence of bromo organic compounds or in the reaction with bromoacetaldehyde diethylacetal which gives a yellow precipitate. Benzene was evaporated from the organic liquid phase and the residue was subjected to PLC plates on column chromatography to separate the products using the proper eluent.

PTC Alkylation of pyrazolone (1) by benzyl bromide:

a) In the absence of carbon disulphide: a colourless oil was obtained which was separated into 1.2 g (34%) of **2** and unreacted pyrazolone (1) by column chromatography using n-hexane / ethyl acetate (5:1) as eluent.

4,4-Dibenzyl-3- methyl-1-phenyl-2- pyrazolin-5-one (**2**) : colourless oil - Anal. Calcd for $C_{24}H_{22}N_2O$; C, 81.33 ; H, 6.26 ; N ,7.90 . Found : C, 81.21 ; H, 6.29 ; N, 8.02 - IR (film): ν (cm^{-1}) = 2847-3086 (CH), 1701 (C=O), 1595 (C=C, C=N) - ^{1}H- NMR : δ =2.13 (s, 3H, $C\underline{H}_3$), two AB systems, δ_A = 3.39, δ_B=2.98, I^2JI = 13.6 Hz, $C(C\underline{H}_2)_2$, 7.07-7.72 (m, 15H, Ar-$\underline{H}$) - ^{13}C-NMR: δ (ppm)= 15.04 ($\underline{C}H_3$), 41.33 ($\underline{C}H_2)_2$, 119.86, 125.29, 127.27, 128.39, 128.58, 129.03 (aromatic $\underline{C}$-H), 134.82 (two phenyl-C-1), 137.30 (N- phenyl-C-1), 160.85 (C-3), 174.56 (C-5) - MS : m/z (%) = 354(9) [M^+], 265 (5), 264 (24) , 263 (4), 173(7), 105(4), 106(3), 92 (9), 91 (100), 85 (9), 77 (20), 71 (15), 65 (5), 57 (22), 43 (14).

b) In the presence of carbon disulphide : 0.25 g of **3** and 1.2 g (48%) of **4** were obtained after separation by PLC using cyclohexane/ ethyl acetate (4:1) as elueut.

5- Benzyloxy-3- methyl-1- phenyl-1H- pyrazole (**3**) : colourless oil - Anal. Calcd for $C_{17}H_{16}N_2O$; C, 77.25 ; H, 6.10 ; N, 10.60 . Found : C, 77.12 ; H, 6.09 ; N, 10.50 - IR (film): ν (cm^{-1}) = 2875 - 3136 (CH), 1591 (C=C, C=N)- ^{1}H- NMR : δ (ppm) = 2.24 (s, 3H, $C\underline{H}_3$), 5.04 (s, 2H, $OC\underline{H}_2$) , 5.49 (s, 1H, 4-$\underline{H}$), 7.17-7.97 (m, 10H, Ar-$\underline{H}$) - ^{13}C- NMR: δ (ppm) = 14.55 ($\underline{C}H_3$), 73.61 ($OC\underline{H}_2$), 87.06 (C-4), 121.72 , 125.75, 127.34, 128.35, 128.60, 128.75 (aromatic $\underline{C}$-H), 135.48 (two phenyl-C-1), 138.74 (N-phenyl-C-1), 148.63 (C-3), 154.48 (C-5) - MS : m/z (%) = 265(6) [M^++1], 264(33) [M^+], 173(10), 106(4), 105(4), 92(11), 91(100), 77(24), 65(6).

4- (bis-Benzylthio)-methylene-3-methyl-1- phenyl-2- pyrazolin-5- one (**4**) : red crystals from n- hexane - mp 119 °C - Anal. Calcd for $C_{25}H_{22}N_2S_2O$; C, 69.74 ; H, 5.15 ; N, 6.51 . Found : C, 69.54 ; H, 5.16 ; N, 6.42 - IR (KBr): ν (cm^{-1}) = 2825- 3020 (CH), 1656 (C=O), 1595 (C=C, C=N) - ^{1}H-NMR : δ (ppm)= 2.33 (s, 3H, CH_3), 4.33 (s, 2H, S- CH_2), 4.44 (s, 2H, S- CH_2), 7.13-7.99 (m, 10H, Ar-H)- ^{13}C-NMR : δ (ppm) = 17.69 (CH_3), 41.67 (S-CH_2), 42.72 (S-CH_2), 118.95, 123.19, 124.63, 127.76, 128.88, 129.25, 129.43 (aromatic C-H), 135.46 (phenyl-C-1), 135.73 (C-4), 138.53 (N-phenyl-C-1), 147.06 (C-3), 160.54 (CS_2), 169.42 (C-5) - MS : m/z (%) = 430(6) [M^+], 339(5), 246(7), 218(5), 217(30), 216 (16), 215(6), 181(4), 124(12), 121(4), 92(13), 91 (100), 77(6), 76(4), 65(13), 45(6).

PTC- Alkylation of pyrazolone (1) by 1,3- dibromopropane:

a) In the absence of carbon disulphide : a mixture resulted, which was separated into 0.32 g (17%) of **5** and 1.35 g (46%) of **6** by PLC plates using n- hexane /ethyl acetate (5:1) as eluent.

1,3-Di- (3-methyl-1-phenyl-1H- pyrazol-5-yloxy) propane (**5**) : pale yellow crystals from n- hexane - mp 68 °C - Anal. Calcd for $C_{23}H_{24}N_4O_2$; C, 71.11 ; H, 6.23 ; N, 14.42 . Found : C, 70.98 ; H, 6.25 ; N, 14.29 - IR (KBr): ν(cm^{-1}) = 2924- 3137 (CH), 1591 (C=C, C=N) - ^{1}H- NMR: δ (ppm) = 2.26 (s, 6H, two CH_3), 2.27 (m, 2H, C- CH_2-C), 4.19 (t, 4H, two O-CH_2, J = 6.1 Hz), 5.44 (s, 2H, two 4- H), 7.19- 7.92 (m, 10H, Ar-H)- ^{13}C- NMR : δ (ppm) = 14.55 (two CH_3), 28.62 (C-CH_2-C) , 68.13 (two O-CH_2), 86.51 (two C-4), 121.87, 125.95, 128.81 (aromatic C-H), 138.61 (N- phenyl-C-1), 148.77 (C-3), 154.35 (C-5) - MS : m/z (%) = 389(5) [M^++1], 388(19) [M^+], 296(17), 294(17), 216(15), 215(100), 214 (59), 187(30), 186(34), 185(24), 174(48), 173(38), 149(16), 113(11), 106(11), 105(16), 99(14), 97(14), 91(12), 85(31), 83(14), 77(65), 71(43), 69(13), 57(53), 55(14), 43(21), 41(19).

1-Bromo-3-(3- methyl-1- phenyl-1H-pyrazol-5- yloxy) propane (**6**) : colourless oil - Anal. Calcd for $C_{13}H_{15}N_2OBr$; C, 52.90 ; H, 5.12 ; N, 9.49 . Found : C, 53.07 ; H, 5.22 ; N, 9.60 - IR (film): $\nu(cm^{-1})$ = 2953- 3137 (CH), 1591 (C=C, C=N)- ^{1}H- NMR : δ (ppm)= 2.27 (s, 3H, CH_3) , 2.32 (m, 2H, C-CH_2-C), 3.51 (t, 2H, -CH_2-Br, J = 6.3Hz), 4.21 (t, 2H, CH_2-O, J = 6.3Hz), 5.52 (s, 1H, 4-H), 7.21-7.72 (m, 5H, Ar-H)- ^{13}C-NMR: δ (ppm) = 14.56 (CH_3), 29.34 (C-CH_2C) , 31.82 (Br-CH_2), 69.37 (O-CH_2), 86.52 (C-4), 121.85, 125.93, 128.81 (aromatic-CH), 138.66 (N-phenyl-C-1), 148.76 (C-3), 154.35 (C-5) - MS : m/z (%) = 296(57) [M^++1], 295(10) [M^+], 294(58), 216(12), 215(70), 187(10), 186(5), 185(6), 175 (15), 174 (100), 173(78), 129(12), 106(17), 105(19), 91(20), 78(9), 77(71), 41(24).

b) In the presence of carbon disulphide: Separation of the residue by column chromatography using ether/ petroleum ether (1:3) as eluent, gave 0.3 g (10%) of **6** and 1.8 g (62%) of **7**.

4-(1,3-Dithian-2-ylidene)-4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H- pyrazole (**7**): pale yellow crystals from cyclohexane - mp 161°C - Anal. Calcd for $C_{14}H_{14}N_2OS_2$; C, 57.90 ; H, 4.86 ; N, 9.65 . Found : C, 57.92 ; H, 4.94 ; N, 9.72 - IR (KBr): ν (cm^{-1}) = 2853-3074 (CH), 1653 (C=O) - ^{1}H-NMR : ν (ppm) = 2.32 (m, 2H, 5`-$H_2$), 2.49 (s, 3H, $CH_3$), 3.09 (m, 4H, 4`- H_2, 6`- $H_2$), 7.13 - 7.99 (m, 5H, Ar-H) -$^{13}$C- NMR: δ (ppm) = 18.64 ($CH_3$), 23.53 (C-5`), 28.91, 29.84 (C-4`, C-6`), 118.71 (C-4), 121.73, 124.31, 128.66 (aromatic- CH), 138.68 (N-phenyl- C-1), 146.07 (C-3), 162.02 (C-5), 172.70 (C-2`) - MS : m/z (%) = 290(100)[M^+], 243(30), 230(19), 217(11), 216(47), 215(44), 185(17), 91(25), 83(24).

PTC- Alkylation of pyrazolone (1) by methyl bromoacetate:

a) In the absence of carbon disulphide: 0.73 g (30%) of **8** and 0.92 g (29%) of **9** were collected after separation by PLC plates using cyclohexane / ether (2:3).

Methyl (3-methyl-1-phenyl-1H-pyrazol-5-yloxy)acetate (**8**) : pale yellow crystals from cyclohexane - mp 74 °C - Anal. Calcd for $C_{13}H_{14}N_2O_3$; C, 63.41 ; H, 5.73 ; N, 11.38 . Found : C, 63.28 ; H, 5.72 ; N, 11.31 - IR (KBr): ν (cm^{-1})= 2953- 3139 (CH), 1752 (C=O ester), 1591 (C=C, C=N)- ^{1}H-NMR : δ (ppm)= 2.27 (s, 3H, CH_3), 3.83 (s, 3H, CO_2CH_3), 4.70 (s, 2H, OCH_2), 5.53 (s, 1H, 4-H), 7.2- 7.93 (m, 5H, Ar-H) - ^{13}C-NMR : δ (ppm) = 14.56 (CH_3), 52.46 (OCH_3), 68.03 (OCH_2), 86.59 (C-4), 122.12, 126.18, 128.83 (aromatic CH), 138.44 (N-phenyl- C-1), 148.65 (C3), 153.64 (C-5), 168.06 (- CO_2) - MS : m/z (%) = 247(20)[M^++1], 246(98) [M^+], 215(6), 187(13), 174(19), 173(100), 118(4), 106(16), 105(16), 91(6), 78(6), 77(68).

Methyl [5-(methoxycarbonylmethoxy)-3-methyl-1-phenyl-1H-pyrazol-4-yl]acetate (**9**) : yellow oil - Anal.Calcd for $C_{16}H_{18}N_2O_5$; C, 60.37 ; H, 5.70 ; N, 8.80 . Found : C,60.45 ; H,5.75 ; N,8.91- IR (film): ν(cm^{-1})= 2848- 2999 (CH), 1735, 1740 (C=O ester), 1599 (C=C, C=N) - ^{1}H-NMR : δ (ppm) = 2.23 (s, 3H, CH_3), 3.50 (s, 2H, 4-CH_2), 3.71 (s, 6H, two OCH_3), 4.52 (s, 2H, OCH_2), 7.26-7.83 (m, 5H, Ar-H) - ^{13}C-NMR : δ (ppm) = 12.83 (CH_3), 28.24 (4-CH_2), 52.09 (OCH_3), 70.29 (OCH_2), 122.18, 126.71,129.14 (aromatic CH), 138.37 (N- phenyl-C-1), 148.26 (C-4), 150.57 (C-3), 168.55 (C-5), 171.77 (two CO_2- ester) - MS : m/z (%)= 319(12) [M^++1], 318(59) [M^+], 260 (21), 259 (100), 246 (5), 245 (23), 213 (5), 199 (15), 187 (7), 186 (45), 185 (15), 92 (7) , 77 (22) .

b) In the presence of carbon disulphhide: Separation of the residue by PLC plates using cyclohexane/ ethyl acetate (1:1)as eluent, gave 0.3 g (21%) of **8** and 1.2 g (53%) of **10** as red oil.

4-[Bis(methoxycarbonylmethylthio)methylene]-4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H - pyrazole (**10**) : Anal. Calcd for $C_{17}H_{18}N_2S_2O_2$; C, 51.76 ; H, 4.60 ; N, 7.10 . Found : C,51.93 ; H,4.56 ; N,7.05 - IR (film): ν (cm^{-1}) = 2849-2953 (CH), 1738 (C=O ester), 1670 (C=O), 1596 (C=C, C=N) - ^{1}H-NMR : δ (ppm)= 2.56 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3),

4.11 (s, 2H, $SC\underline{H}_2$), 4.15 (s, 2H, $SC\underline{H}_2$), 7.17-7.95 (m, 5H, Ar-H) - ^{13}C-NMR : δ (ppm)= 17.95 ($\underline{C}H_3$), 38.08 ($S\underline{C}H_2$), 39.13 ($S\underline{C}H_2$), 52.88 ($O\underline{C}H_3$) , 53.11 ($O\underline{C}H_3$), 124.99 (C-4), 118.97,124.88, 128.78 (aromatic C-H), 138.21 (N-phenyl-C-1), 147.28 (C-3), 160.01 (=$\underline{C}S_2$-), 166.42 (C-5), 168.41 (-$\underline{C}O_2$), 168.62 (-$\underline{C}O_2$) - MS : m/z (%) = 394 (8) [M^+], 318(16), 259(33), 254(13), 246(38), 236(21), 232(14), 210(41), 204(27), 186(16),179(11), 178 (57), 177(14), 174(12), 173(45), 151(28), 149(32), 147(17), 146(64), 121(12), 119(40), 118(22), 114 (16), 106(29), 105(27), 104(14), 103(16), 95(11), 91(23), 85(15), 77(37), 74(24), 73(18), 71(20), 59 (33), 57(26), 47(15), 46(18), 45(100), 42(18).

PTC- Reaction of pyrazolone (1) with bromoacetaldelyde diethylacetal:

a) In the absence of carbon disulfhide: An orange solid was abtained which was separated into 0.9 g (25%) of **11** and unreacted pyrazelone (**1**) by column chromatography using n-hexane / ethyl acetate (4:1) as eluent.

4,4'-Methine-bis-(3-methyl-1-phenyl-2-pyrazolin-5-one) (**11**) : Orange crystals from n- hexane - mp 185 °C - Anal. Calcd for $C_{21}H_{18}N_4O_2$; C, 70.38 ; H, 5.06 ; N15.63 . Found : C, 70.58 ; H, 5.12 ; N, 15.81 - IR (KBr): ν (Cm^{-1}) = 2923-3064 (CH), 1625 (C=O), 1591 (C=C, C=N) - ^{1}H-NMR: δ (ppm) = 2.35 (s, 6H, two $C\underline{H}_3$), 7.23-7.91 (m, 12H, Ar-H, 4'-H, 4- C<u>H</u>=) - ^{13}C-NMR : δ (ppm) = 12.88 (two $\underline{C}H_3$), 109.47 (C-4'), 121.05, 126.51, 128.86 (aromatic C-H), 138.24 (N-phenyl- C-1) , 152.67 (C-3), 161.23 (C-5) - MS : m/z(%)= 359 (25) [M^++1], 358 (100) [M^+], 341 (28), 266 (9), 118 (8), 91 (22), 77 (22).

b) In the presence of carbon disulphide: The residue of the liquid phase was separated by PLC plates into 0.33 g (9%) of **11** and unreacted pyrazolone (**1**) while 1.15 g (46%) of **12** was precipitated after acidification of potassicum carbonate solution as yellow solid.

(4,5-Dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)dithiocarboxylic acid (**12**) : yellow crystals from petroleum ether - mp 107 °C . Anal. Calcd for $C_{11}H_{10}N_2S_2O$; C, 52.78 ; H, 4.03 ; N, 11.19 . Found : C, 53.00 ; H, 4.10 ; N, 11.23 - IR : n (cm^{-1}) = 2919-3051 (CH), 2361 (SH), 1610 (C=S, C=O) , 1594 (C=C, C=N) - ^{1}H-NMR : d (ppm)= 2.61 (s, 3H, CH_3), 5.61 (s,1H, 4-H), 7.25-7.83 (m, 5H, Ar-H), 13.44 (s, 1H, CS_2H) - ^{13}C-NMR : d (ppm) = 16.82 (CH_3), 112.11 (C-4), 121.58, 127.33, 129.10 (aromatic C-H) , 136.73 (N-phenyl-C-1), 147.14 (C-3), 158.22 (C-5), 207.59 (4-CS_2H) - MS : m/z (%) = 252(9) [M^++2], 251 (13) [M^++1], 250(83)[M^+], 218(23), 217(99), 216(100), 215(39), 174(22), 105(10), 92(24), 91(48), 83(17), 77(46), 76(17), 65(15), 51(10).

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