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# Pyrazole Studies

## VI *. Variation of the Basic Properties of Pyrazolones with Substitution in the Pyrazolone Nucleus

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The p$K_B$-values of a series of substituted pyrazolones have been determined by potentiometrical titration with perchloric acid in glacial acetic acid.

It is shown that electron releasing and electron attracting groups as substituents at different positions in the pyrazolone nucleus have an effect on the p$K_B$-values, in opposite direction when placed at $N_1$ or $C_2$, in the same direction when placed at $C_4$, the value of p$K_B$ being partly determined by the participation of the polar phenol betain structure in the total resonance hybride. Only when the pyrazolone has the possibility of acquiring an antipyrin structure (*i.e.* only when it is not doubly substituted at $C_4$) is it possible to determine the p$K_B$-value in the way described.

The dipole moment of 3-antipyrin (1-phenyl-2 : 5-dimethylpyrazol-3-one) and 1-phenyl-3-methoxy-5-methylpyrazole have been measured. The value found for 3-antipyrin shows that the polar phenol betain structure is more abundantly represented in this substance than in the isomeric antipyrin (1-phenyl-2 : 3-dimethyl-pyrazol-5-one). The values found for p$K_B$ of the two substances corroborate this result.

In a previous paper (Veibel *et al.*[1]) we showed that it is possible to determine p$K_B$ for substituted pyrazolones by titrating them with perchloric acid, using glacial acetic acid as solvent. We decided to use this method for investigating the variation of the basic properties of the pyrazolone nucleus with substitution of different hydrocarbon groups for hydrogen, located at the positions 1, 3 or 4. Table 1 gives a summary of the results obtained, included some few pyrazolones where hydrogen at $C_4$ has been substituted with a halogen atom instead of with a hydrocarbon radical.

Remembering that only such pyrazolones which are able to acquire an antipyrin structure are titratable as bases (Veibel *et al.*[1]) we have in Table 1 formulated the pyrazolones as phenol betains, understanding by this the total resonance hybride:

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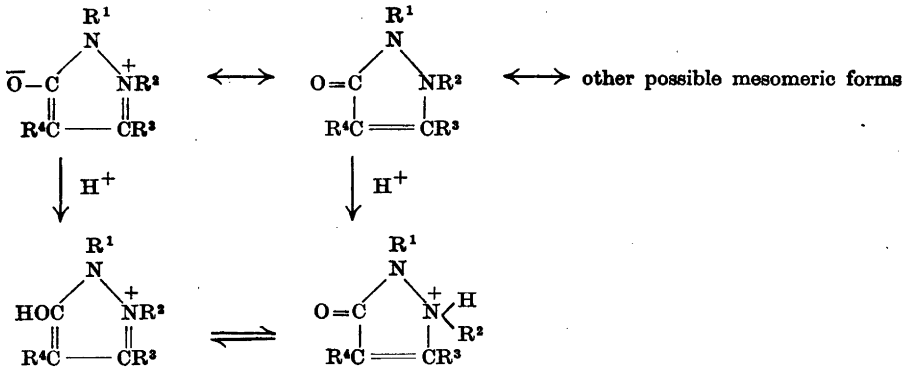
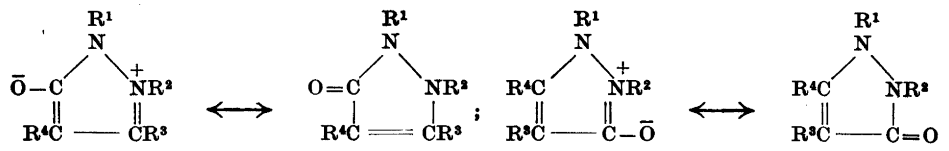



A comparison of I, II, III, and VIII shows that the substitution of a methyl group for hydrogen at $C_3$ increases the basic strength of the pyrazolone (0.6 units in $pK_B$), that of a tertiary butyl group too, but less (0.4 units in $pK_B$), and that of a phenyl group has practically no effect. In terms of the theory of hyperconjugation a methyl group is an electron releasing group, a tertiary butyl group too, but less. The phenyl group, on the other hand, is an electron attracting group. The two alkyl groups will tend to increase the participation of the phenol betain structure in the resonance hybride, thus increasing the basic character of the pyrazolone. The phenyl group might be expected to act in the opposite direction, but the value found for $pK_B$ of VIII gives no indication of either electron releasing or electron attracting effect of the phenyl group at $C_3$. A comparison of II with IV, V and VI shows that substitution of an alkyl group, or an alkenyl group, for a hydrogen atom at $C_4$ slightly reduces the basic character of the pyrazolone. This may mean that an electron releasing group as substituent at the carbon atom which is neighbour to the negative end of the conjugated system of double bonds has an effect in the opposite direction of the effect caused by a similar group at the carbon atom which is neighbour to the positive end of the conjugated system. Regarding the non-polar antipyrine structure it means that an electron releasing substituent at the carbon-end of the conjugated system $O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}$ will increase the basic properties of the pyrazolone, whereas a similar substituent at the neighbouring carbon atom will decrease the basic properties. A comparison of the couples I—VIII and II—VII shows that the effect of a phenyl group as substituent is greater at $C_4$ than at $C_3$. It is seen (II—IV—VII; X—XI—XIV) that the effect of the electron attracting phenyl group at $C_4$ is in the same direction as and somewhat greater than the effect of the electron releasing alkyl groups. Finally, IX shows that substitution of two alkyl groups for two hydrogen atoms at $C_4$, which prohibits the establishing of an antipyrin structure, will cause a weakening of the basic properties of the pyrazolone to such a degree that the substance is untitratable, at all events by the method applied here.

II—X—XV show that the effect of substitution of methyl for hydrogen at the nitrogen atom is a considerable increase of the basic properties. A comparison of the couples I—II and II—X shows that the effect of a methyl

*Table 1. Summary of pyrazolones investigated.*



I—XXVIII: XXIX—XXXIII;

| | $R^1$ | $R^2$ | $R^3$ (at $C^3$) | $R^4$ (at $C^4$) | MV at 50 % neutralisation | $pK_B$ | M.p. found | M. p. lit. |
|---|---|---|---|---|---|---|---|---|
| I | H | H | H | H | 184 | 11.5 | 165° | 165°[2] |
| II | H | H | $CH_3$ | H | 151 | 10.9 | 216—18° | 215°[3] |
| III | H | H | $(CH_3)_2C$ | H | 162 | 11.1 | 200° | 210°[25] |
| IV | H | H | $CH_3$ | $C_2H_5$ | 160 | 11.1 | 227—28° | 228°[4] / 230°[5] |
| V | H | H | $CH_3$ | n-$C_3H_7$ | 167 | 11.2 | 207—08° | 209—10°[6] / 211°[4] |
| VI | H | H | $CH_3$ | $C_3H_5$ | 164 | 11.2 | 195—96° | 195°[7] |
| VII | H | H | $CH_3$ | $C_6H_5$ | 183 | 11.4 | 208—10° | — |
| VIII | H | H | $C_6H_5$ | H | 177 | 11.4 | 232—33° | 236—37°[8] |
| IX | H | — | $CH_3$ | $(C_2H_5)_2$ | >400 | >15 | 104—05° | 105.5°[9] |
| X | $CH_3$ | H | $CH_3$ | H | 119 | 10.3 | 117° | 117° [9a] |
| XI | $CH_3$ | H | $CH_3$ | $C_2H_5$ | 126 | 10.5 | 94—95° | — |
| XII | $CH_3$ | H | $CH_3$ | n-$C_3H_7$ | 127 | 10.5 | 84—85° | — |
| XIII | $CH_3$ | H | $CH_3$ | $C_3H_5$ | 127 | 10.5 | 71—72° | — |
| XIV | $CH_3$ | H | $CH_3$ | $C_6H_5$ | 147 | 10.9 | 175° | — |
| XV | $CH_3$ | H | $C_6H_5$ | H | 150 | 10.9 | 206° | 207° [9b] |
| XVI | $C_6H_5$ | H | $CH_3$ | H | 176 | 11.3 | 127° | 127°[10] |
| XVII | $C_6H_5$ | H | $CH_3$ | $C_2H_5$ | 186[1] / 177[2] | 11.5[1] / 11.3[2] | 111° / 82° | 108°[11] / 80°[11] |
| XVIII | $C_6H_5$ | H | $CH_3$ | n-$C_3H_7$ | 179 | 11.4 | 101—02° | 101—02°[12] |
| XIX | $C_6H_5$ | H | $CH_3$ | $C_6H_5$ | 209 | 11.9 | 199—200° | — |
| XX | $C_6H_5$ | H | $C_6H_5$ | H | 228 | 12.2 | 137° | 137—38°[13] |
| XXIa | $C_6H_5$ | H | $CH_3$ | Cl | 287 | 13.2 | 153° | 153°[14] |
| XXIb | $C_6H_5$ | H | $CH_3$ | Br | 293 | 13.3 | 122° | 122°[14] |
| XXII | $C_6H_5$ | — | $CH_3$ | $CH_3$, Cl | >420 | >15 | 68° | 68°[14] |
| XXIII | $C_6H_5$ | $CH_3$ | $CH_3$ | H | 169 | 11.2 | 113° | 113° |
| XXIV | $C_6H_5$ | $CH_3$ | $CH_3$ | $(CH_3)_2CH$ | 189 | 11.6 | 101—03 | 101—03° |
| XXV | $C_6H_5$ | H | $CH_3$ | pyrazolonyl | 275 | 13.0 | destr. | destr. [15] |
| XXVI | $C_6H_5$ | — | $CH_3$ | $C_3H_5$ pyrazolonyl | >410 | >15 | 161—62° | 161—62°[16] |
| XXVII | $C_6H_5$ / $C_6H_5$ | H / H | $CH_3$ / $CH_3$ | -CH=pyrazolonyl / =CH-pyrazolonyl | 312 / >400 | 13.8 / >15 | 185° | 180°[17] |
| XXVIII | $C_6H_5$ | H | $CH_3$ (at $C_4$) | diphenylethenyl (at $C_5$) | 230 | 12.2 | 220° | — |
| XXIX | $C_6H_5$ | H | H | $CH_3$ | 226 | 12.2 | 167° | 167°[18] |
| XXX | $C_6H_5$ | H | $C_2H_5$ | $CH_3$ | 236 | 12.3 | 172° | 172°[19] |
| XXXI | $C_6H_5$ | H | H | $C_6H_5$ | 273 | 12.9 | 256° | 256°[19] |
| XXXII | $C_6H_5$ | $CH_3$ | H | $CH_3$ | 190 | 11.6 | 113° | 113°[20] |
| XXXIII | $C_6H_5$ | ($OCH_3$ at $C_3$) | H | $CH_3$ | 244 | 12.5 | B.p. 16 mm 154—56° | 150—60°[20] |

[1] Anhydrous. [2] 1 mole of water of crystallisation.

group at $C_3$ and at $N_1$ is sensibly the same. In this series the effect of substitution of hydrogen with alkyl or aryl at $C_4$ or methyl with phenyl at $C_3$ described above is found again.

In XVI—XX the same effect of substituting alkyl or aryl groups for hydrogen at $C_3$ or $C_4$ is observed. Here the effect of a phenyl group at $C_3$ is somewhat greater than at $C_4$. Possibly this is due to some form of interaction between the phenyl groups at $N_1$ and at $C_3$, the $N_2$-atom facilitating the displacement of electrons somewhat more than the $C_5$-atom.

The effect of a phenyl group at $N_1$ is a decrease of the basic properties (compare II and XVI). The change in $pK_B$ is, however, only 0.4, considerably less than the effect of substitution of a phenyl group for a hydrogen atom in *e. g.* aniline (change of $pK_B \sim 3.7$).

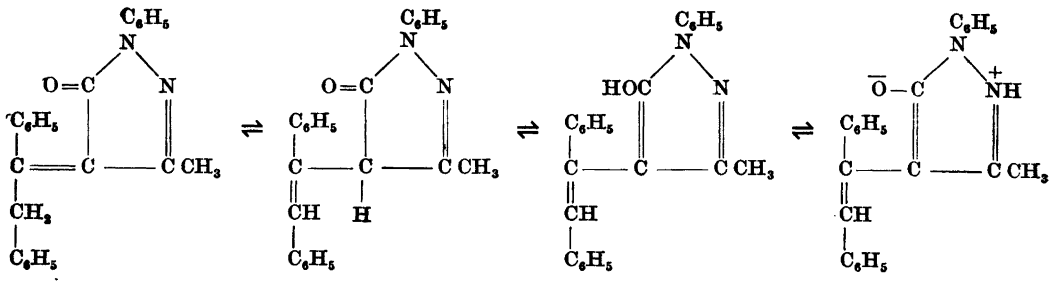
From XXI a and b we learn that the effect of halogen atoms (electron attracting atoms) is considerably greater than the effect of a phenyl group. There is no significant difference between the effect of chlorine and of bromine. XXII verifies the result found in IX, that double substitution at $C_4$ will make the pyrazolone untitratable.

The $pK_B$-value found for antipyrin (XXIII) is in accordance with the assumption that the antipyrin structure (or the phenol betain structure) is responsible for the basic properties of the pyrazolones, $pK_B$ being for antipyrin within the limit of error identical with $pK_B$ for 1-phenyl-3-methylpyrazol-5-one. XXIV shows that the effect of an alkyl-substitution at $C_4$ is the same as that found for monosubstitution at $C_4$ in pyrazolones not substituted at $N_2$.

XXV—XXVIII are examples corroborating the results obtained with less complicated pyrazolones. XXV is the bis-pyrazolone of XVI. It is titratable, but $pK_B$ has increased from 11.3 to 13.0. 1 mole of the bis-pyrazolone claims 2 moles of perchloric acid. XXVI is the bispyrazolone of XVII. As it is doubly substituted at $C_4$ it cannot acquire antipyrin structure and, consequently, it is untitratable.

In XXVII we investigated a bis-pyrazolone with a methin group interposed between the two pyrazolone nuclei. The result is that at $C_4$ we have in one nucleus a double bond, in the other a single bond. The substance claims one mole of perchloric acid per mole of bis-pyrazolone, the $pK_B$ of the molecule being 13.8. It seems natural to locate the basic properties on the pyrazolone nucleus with a single bond to the methin group and to regard the other nucleus as untitratable.

XXVIII is an example of a pyrazolone with double bond to a substituent at $C_4$, *viz.* a 1:2-diphenylethylidene group. The pyrazolone is titratable with perchloric acid and it may also be titrated in ethanolic solution with 0.1 *N* sodium hydroxide, comp. Veibel *et al.*[21]. The titration curves are given in Fig. 1. From the curves the equivalent point may be determined according to Gran[22]. We find equivalent weights 354 and 352, calculated 352.4. The titratability of the substance means that it behaves not as a 1:2-diphenylethylidene, but as a 1:2-diphenylethene-substituted pyrazolone, a hydrogen atom having been transferred from the substituent to the pyrazolone nucleus, creating by this a double bond in the substituent, conjugated with the double bonds in the pyrazolone nucleus:



XXVIII

XXIX—XXXIII are some substituted pyrazol-3-ones. XXIX, XXX and XXXI are isomers of XVI, XVII and XX. It is seen that the $pK_B$-values of the pyrazol-3-ones are superior to the corresponding values for the pyrazol-5-ones by 0.7—0.9, *i. e.* the pyrazol-3-ones are less basic than the pyrazol-5-ones. For the pyrazol-5-ones we have made the assumption that a phenol betain structure is responsible for the basic character of the substances. If this assumption is valid for the pyrazol-3-ones too, it seems natural to consider the fact that the distances between the positive and the negative charges is shorter in the pyrazol-3-ones than in the pyrazol-5-ones. This difference may explain the difference in basic strength.

XXIII and XXXII are antipyrin and 3-antipyrin. Here the difference in $pK_B$ is only 0.4, and whereas the difference between the $pK_B$-values for XVI and XXIII is only 0.1, we find a difference of 0.6 between the $pK_B$-values for XXIX and XXXII. The electron releasing methyl group at $N_2$ in XXXII has caused a considerable increase in the participation of the phenol betain

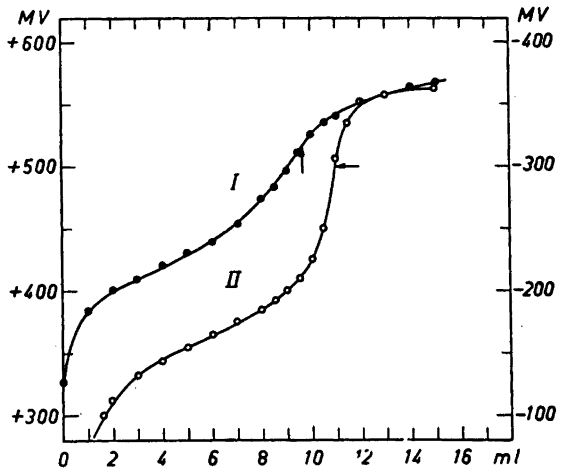
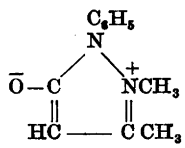



*Fig. 1. Titration curves for XXVIII. I: Titration with 0.1 N perchloric acid (right hand ordinate). II: Titration with 0.1 N sodium hydroxide (left hand ordinate). The arrows indicate the end-points calculated from the curves.*

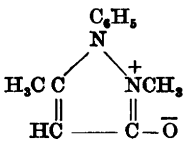
structure in the resonance hybride. A comparison of XXXII and XXXIII, the 3-antipyrin and 1-phenyl-3-methoxy-5-methylpyrazole tends to corroborate the hypothesis discussed here. For XXXIII no phenol betain structure is possible, and not only is the substance less basic than 3-antipyrin, but it is a weaker base than 1-phenyl-5-methylpyrazol-3-one too.

A further corroboration is obtained by comparing the dipole moments of XXXII and XXXIII with that of antipyrin (XXIII). The values found are:



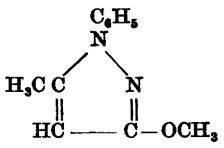
XXIII

5.48 D (25°)[23]



XXXII

5.69 D (24°)



XXXIII

1.80 D (27°)

As above the distance between the electric charges must be greater in XXIII than in XXXII. With the following bond lengths:

C—O 1.43 Å; N—C 1.47 Å; N—N 1.40 Å; N = C 1.23 Å[24]

and the valence angle 110° (Jensen and Friediger [23]) the distance is approximately 3.77 Å in XXIII and < 2.66 Å in XXXII. Jensen and Friediger estimate from the value of the dipole moment of XXIII that the participation of the phenol betain structure in the resonance hybride is 30—35 %. As the value calculated for the dipole moment of XXXII must be smaller than that calculated for XXIII and a greater value is actually found, this means that the participation of the phenol betain structure in the resonance hybride of XXXII is considerably greater than 35 %.

## EXPERIMENTAL PART

The substances I, II, IV—VI, VIII, IX, XVI—XX, XXV—XXVII and XXIX—XXXIII were prepared by current methods and showed with a few exceptions the m. p. s indicated in the litterature. XXIa, XXIb and XXII were placed at our disposal by Gunnel Westöö, Ph. D., to whom we want to express our thanks. XXIII and XXIV were commercial products. The other substances were prepared as indicated below (all m. p.s are uncorrected; all microanalyses by Mr. A. Grossmann or Mr. W. Egger, Department of Organic Chemistry, The University, Copenhagen).

*3-tert. Butylpyrazol-5-one (III).* 10 ml of ethanol were added to a mixture of 7.5 g of ethyl trimethylacetoacetate (ethyl pivalylacetate) and 4 ml of 60 % hydrazine hydrate. A clear solution resulted. The reaction between the keto ester and hydrazine starts slowly at room temperature, causing a slight increase in temperature and a deposition of crystals. After 2—3 hours the crystals are filtered off, washed with water and air-dried. Yield 4.2 g with m.p. 200° (Dayton [24] indicates m.p. 210° without describing the synthesis). Recrystallised from aqueous ethanol 5.1 g with m.p. 200—201° = 82 % were obtained. (Found: N 20.18. Calc. for $C_7H_{12}ON_2$ (140.2): N 19.99.)

*3-Methyl-4-phenylpyrazol-5-one (VII).* 7.5 g of 50 % hydrazine hydrate are added to 15.4 g of ethyl α-phenylacetoacetate. Some ml of ethanol are added in order to increase the mutual solubility of the components. Upon slight heating the reaction starts and proceeds then regularly. After cooling a raw product was isolated by suction (30 %,

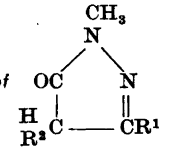
m.p. 208—210°), washed with ethanol and recrystallised from the minimum amount of ethanol. The m.p. was unchanged 208—210°, the yield of pure product was 3.5 g = 27 %. (Found: C 68.96; H 5.69; N 16.13. Calc. for $C_{10}H_{10}ON_2$ (174.2): C 68.92; H 5.78; N 16.09.)

*1-Methyl substituted pyrazol-5-ones (X—XV).* For the preparation of these pyrazolones an aqueous *N* solution of methyl hydrazine was prepared as ollows: A suspension of 1 mole of barium hydroxide octahydrate in 500 ml of water was heated to 100° with mechanical stirring. A solution of 1 mole of hydrazine sulphate in 150 ml of water was heated to 70° and added to the suspension of barium hydroxide, precipitating barium sulphate immediately. In order to complete the precipitation and to obtain the barium sulphate in a filtratable form 300 ml of water was added and the suspension stirred at 70° for a further hour, after which the barium sulphate was filtered off and washed on the filter with hot water, the filtration flask being chilled in ice-water in order to reduce the loss of methyl hydrazine during the filtration. The combined filtrate and washings were made up with water to 1 000 ml. This stock solution was used for the preparation of the 1-methyl-pyrazolones.

A mixture of 0.2 mole of (α-substituted) ethyl acetoacetate or ethyl benzoylacetate and 200 ml *N* methyl hydrazine solution is heated to 70° and mechanically stirred for the time indicated in Table 2. After cooling the solution is extracted twice with low boiling ligroin; from the aqueous layer the water is removed *in vacuo* at a bath temperature of 45—50°. The residue is dissolved in chloroform and dried with anhydrous sodium sulphate. The crude pyrazolone is isolated by evaporation of the chloroform; it is purified by fractionation in a vacuum, preferably from a sausage flask, by recrystallisation from ethyl acetate, methanol or ethanol, or by sublimation.

*1,4-Diphenyl-3-methylpyrazol-5-one* (XIX). 4 g of ethyl α-phenylacetoacetate and 2 g of phenylhydrazine are mixed, forming a homogenous mixture which soon becomes turbid, the mixture at the same time heating up to become luke-warm. When again cooled down to room temperature it solidifies to a semi-solid mass which is dissolved in 25 ml of ethanol. The solution is cooled in ice water, depositing crystals which are filtered off. Yield 3.1 g with m.p. 88—90° (dec.); from the filtrate 1.2 g of crystals with m.p.

*Table 2. Preparation of*



| | $R^1$ | $R^2$ | Reaction time, h. | Yield % | Purified by | M.p. | B.p. | % C | | % H | | % N | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Calc. | found | Calc. | found | Calc. | found |
| X | $CH_3$ | H | 0.5 | 51 | dest. | 117° | $130°_{19mm}$ | — | — | — | — | — | — |
| XI | $CH_3$ | $C_2H_5$ | 10 | 60 | recryst. ethyl ac. | 94—95° | $137°_{15mm}$ | 59.95 | 59.91 | 8.63 | 8.48 | 19.99 | 19.85 |
| XII | $CH_3$ | $C_3H_7$ | 10 | 65 | recryst. ethyl ac. | 84—85° | $150_{15mm}$ | 62.30 | 62.33 | 9.15 | 9.09 | 18.17 | 18.18 |
| XIII | $CH_3$ | $C_3H_5$ (allyl) | 5 | 50 | recryst. | 71—72° | — | 63.12 | 63.15 | 8.02 | 7.90 | 18.41 | 18.42 |
| XIV | $CH_3$ | $C_6H_5$ | 10 | 70 | recryst. aq. methanol | 175° | — | 70.19 | 70.40 | 6.43 | 6.33 | 14.89 | 14.72 |
| XV | $C_6H_5$ | H | 10 | 65 | recryst. ethanol | 206° | — | — | — | — | — | — | — |

198—199°, recrystallised from ethanol 199—200° were isolated. The low melting product is the phenylhydrazone of ethyl α-phenylacetoacetate, the high melting substance is the corresponding pyrazolone. Total yield 76 % (52 % phenylhydrazone and 24 % pyrazolone). (Phenylhydrazone of ethyl α-phenylacetoacetate, Found: C 72.63; H 6.90; N 9.37. Calc. for $C_{18}H_{20}O_2N_2$ (296.4): C 72.94; H 6.80; N 9.45.)

The phenylhydrazone looses ethanol spontaneously, being converted into the pyrazolone, slowly at room temperature (some days), fast at 140° where 0.8968 g loose 0.1376 g during 5 hours, then retaining its weight on prolonged heating. The loss is 15.35 %; calculated for the loss of 1 mole of ethanol 15.55 %.

The pyrazolone may be prepared without isolation of the phenylhydrazone by heating the mixture of ethyl α-phenylacetoacetate and phenylhydrazine to 140° for 1 hour as soon as the spontaneous reaction is over. Yield from 4 g of ethyl α-phenylacetoacetate and 2 g of phenylhydrazine 3.2 g = 64 %. (1,4-Diphenyl-3-methylpyrazol-5-one, Found: C 76.95; H 5.72; N 11.34. Calc. for $C_{16}H_{14}ON_2$ (250.3): C 76.79; H 5.64; N 11.19.)

*1-Phenyl-3-methyl-4(1″:2″-diphenylethenyl)pyrazol-5-one* (XXVIII). This substance is prepared by heating equimolar amounts of 1-phenyl-3-methylpyrazol-5-one and desoxybenzoin on the steam bath for 3—4 hours. The solid condensation product is filtered off, washed with ether (to remove unreacted desoxybenzoin) and recrystallized from glacial acetic acid. Yield 50 %, m.p. 220°. (Found: C 80.90; H 5.79; N 7.99. Calc. for $C_{24}H_{20}ON_2$ (352.4); C 81.79; H 5.72; N 7.95.)

*Determination of the dipole moments of 1-phenyl-2 : 5-dimethylpyrazol-3-one* (XXXII) *and 1-phenyl-3-methoxy-5-methylpyrazole* (XXXIII), Table 3. Thanks are due to Mr. G. Nygaard, M.Sc., and Professor K. A. Jensen, Department of Organic Chemistry, University of Copenhagen, for carrying out the measurements and the calculation of the dipole moments.

*Table 3. Dipole moments of XXXII and XXXIII.*

| | Mole fraction of substance | $d$ of the solution | $\varepsilon$ | $P$ | |
|---|---|---|---|---|---|
| XXXII $M$ = 188.2 | 0.00974 | 0.8784 | 2.7192 | 638.5 | $T$ = 24° $P^\infty$ = 730 $P_E$ (calc.) = 50.7 $P^\infty_{0+A}$ = 679; $P^\infty_0$ = 672 ($P_A$ presumed to be 15 % of $P_E$) |
| | 0.00468 | 0.8753 | 2.4914 | 679.3 | |
| | 0.00238 | 0.8741 | 2.3879 | 719.9 | |
| | $\mu = 0.01273\ \sqrt{P^\infty_0 \cdot T} = 5.69$ D | | | | |
| XXXIII $M$ = 188.2 | 0.0302 | 0.8879 | 2.4845 | 122.9 | $T$ = 27° $P^\infty$ = 127 $P_E$ (calc.) = 52 $P^\infty_{0+A}$ = 75; $P^\infty_0$ = 67 ($P_A$ presumed to be 15 % of $P_E$) |
| | 0.0220 | 0.8824 | 2.4243 | 124.0 | |
| | 0.0151 | 0.8760 | 2.3778 | (133.5) | |
| | $\mu = 0.01273\ \sqrt{P^\infty_0 \cdot T} = 1.80$ D | | | | |

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