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REACTIVITY OF UNSATURATED CENTRES IN HETEROCYCLES AND CHALKONES TOWARD DIAZOALKANES

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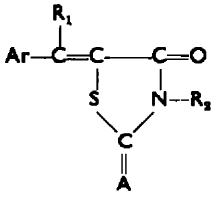
Abstract—Treatment of 4-arylidene derivatives of five-membered heterocycles with diazomethane results in cyclopropane formation; C-alkylation has been observed in the case of 4-ethylidene-2-phenyl-5-(4H)-oxazolone.

Δ^2-Pyrazolines have been obtained via the action of diazomethane on a number of newly prepared chalkones; cyclopropane formation is proved in the case of piperonylidene-5-acetoacenaphthene.

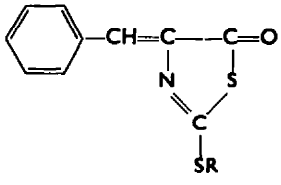
Methylation of 4-arylazo derivatives of a number of five-membered heterocycles is discussed.

DIAZOALKANES have been added to a large number of conjugated olefins. Numerous cases have been cited in which cyclopropanes result when pyrazolines are decomposed thermally.[1] Simple pyrazolines often produce olefinic products while more complex pyrazolines generally give cyclopropanes.[2]

The addition of diazoalkanes to the conjugation created by the attachment of an exocyclic C=C bond to a heterocyclic ring having a carbonyl function seems not to have been fully investigated.[3] Recently, Mustafa *et al.*[4] reported the "C-alkylation" of Ia to Ib, without the isolation of the corresponding pyrazolines.



Ia, $R_1 = H$; $A = O$; $R_2 = C_6H_5$
b, $R_1 = CH_3$; $A = O$; $R_2 = C_6H_5$
c, $R_1 = R_2 = H$; $A = S$; $Ar = C_6H_5$
d, $R_1 = H$; $R_2 = CH_3$; $A = S$.



IIa, R = H (or tautomer)
b, $R = CH_3$

[1] Ed. Buchner, *Liebigs Ann.* **273**, 229 (1893); D. Gotkis and J. B. Cloke, *J. Amer. Chem. Soc.* **56**, 2710 (1934).

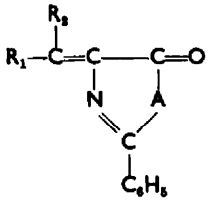
[2a] *Newer Methods of Preparative Organic Chemistry*, p. 552. Interscience, New York (1948); [b] von K. Auwers and F. Konig, *Liebigs Ann.* **496**, 252 (1932); [c] Th. Wieland and O. Probst, *Ibid.* **530**, 277 (1937); [d] H. N. Raydon, *J. Chem. Soc.* 829 (1936); [e] D. W. Adamson and J. Kenner, *Ibid.* 1551 (1937); [f] A. Mustafa and M. K. Hilmy, *Ibid.* 1434 (1952); [g] L. Horner and E. Lingnau, *Liebigs Ann.* **591**, 21 (1955); [h] K. D. Gundermann and R. Thomas, *Chem. Ber.* **93**, 883 (1960); [i] F. M. Dean, P. G. Jones and P. Sidisunthorn, *J. Chem. Soc.* 5186 (1962); [j] G. Adametz, G. Billek, A. Eitel, O. E. Polansky, O. Saiko, J. Swoboda and F. Wessely, *Monatsh.* **94**, 334 (1963); [k] M. Alguero, J. Bosch, J. Castanar, J. Castella, J. Castello, R. Mestres, J. Pascual and F. Serratosa, *Tetrahedron* **18**, 1381 (1962).

[3] R. Gompper, *Recent Advances in Heterocyclic Compounds* (Edited by A. R. Katritzky) Vol. 2; p. 251. Academic Press, New York (1963).

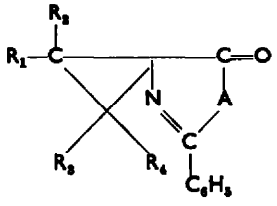
[4] A. Mustafa, W. Asker and M. E. Sobhy, *J. Amer. Chem. Soc.* **82**, 2597 (1960).

On the other hand, the exocyclic double bond in Ic and IIa appears stable toward the action of ethereal diazomethane and only (Id)[5] and (IIb)[6] are formed, respectively.

In continuation of previous work,[4,6] cyclopropane formation now has been observed upon treatment of IIIb with ethereal diazomethane yielding IVb. In contrast to the behaviour of Ic toward the action of diazomethane,[5] N-methylation as well as cyclopropane formation (cf. IVa) was observed upon treatment of IIIa with the same reagent.

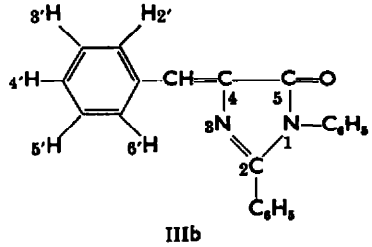


IIIa, $R_1 = C_6H_5$; $R_2 = H$; A = NH
b, $R_1 = C_6H_5$; $R_2 = H$; $A = NC_6H_5$
c, $R_1 = C_6H_5$; $R_2 = H$; A = O
d, $R_1 = CH_3$; $R_2 = H$; A = O
e, $R_1 = R_2 = CH_3$; A = O
f, $R_1 = 1\text{-}C_{10}H_7$; $R_2 = H$; A = O
g, $R_1 = C_6H_4OCH_3\text{-}p$; $R_2 = H$; A = O
h, $R_1 = C_6H_3O_2\text{:}CH_2$ (3:4); $R_2 = H$; A = O
i, $R_1 = C_6H_5$; $R_2 = H$; A = S
j, $R_1 = C_6H_4Cl\text{-}p$; $R_2 = H$; A = S



IVa, $R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$; $A = NCH_3$
b, $R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$; $A = NC_6H_5$
c, $R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$; A = O
d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$; A = O
e, $R_1 = 1\text{-}C_{10}H_7$; $R_2 = R_3 = R_4 = H$; A = O
f, $R_1 = C_6H_5$; $R_2 = H$; R_3 and $R_4 = C_{12}H_8$; A = O
g, $R_1 = C_6H_4OCH_3\text{-}p$; $R_2 = H$; R_3 and $R_4 = C_{12}H_8$; A = O
h, $R_1 = C_6H_3O_2\text{:}CH_2$(3:4); $R_2 = H$; R_3 and $R_4 = C_{12}H_8$; A = O
I, $R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$; A = S
j, $R_1 = C_6H_4Cl\text{-}p$; $R_2 = R_3 = R_4 = H$; A = S
k, $R_1 = C_6H_4Cl\text{-}p$; $R_2 = H$; R_3 and $R_4 = C_{12}H_8$; A = S

The NMR spectrum of IVb reveals an ABX system. The assignments of chemical shifts are summarized in Table 1. The spectrum of IIIb was run for comparison of chemical shifts under identical conditions.



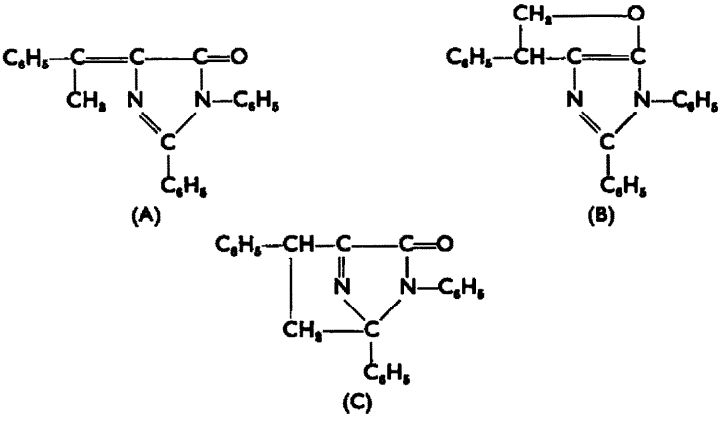
IIIb

[5] D. J. Dijksman and G. T. Newbold, *J. Chem. Soc.* 1213 (1951).
[6] A. Mustafa and M. M. M. Sallam, *J. Org. Chem.* **26**, 1782 (1961).

TABLE 1

Compound	τ	Intensity	Multiplicity	Assignment
IIIb	2·65	14	complex	1-Ph, 2-Ph, —CH═, 3′-, 4′-, 5′-H's.
	1·73	2	ca. double doublet	2′-, 6′-H's.
IVb	7·64	2	AB part of an ABX system, J_{AB} = 5 c/s	N—C—C—H (vic. because small J).
	7·63			
	6·72	1	quartet; X part of an ABX system	CH unequally coupled to two other protons.
	ca. 2·75	15	complex	three Ph groups.

It can be seen that the phenyl groups at the 1- and 2-positions in IIIb must be twisted out-of-plane of the heterocyclic ring because of steric interference. These phenyl groups would be expected to give compact signals, as does *cis*-stilbene in comparison to the planar *trans*-stilbene.[7,8a] The benzylidene group should be coplanar with the heterocyclic ring; and in agreement there is a complex two-proton signal at low field. This must arise from the two *o*-protons (2′- and 6′-) which are deshielded partly by the adjacent double-bond and partly by the hetero-ring. The lone —CH═ proton, not being coupled to another must give a single line, but this is evidently submerged in the main signal from the phenyl groups, which integrates as 14 protons, relative to 2 for the low-field signal.



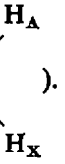
The PMR spectrum of IVb definitely excludes structure (A) because there is no singlet of intensity (3H) in the spectrum. There are two groups of lines which constitute an ABX spin–spin system,[9] indicating the grouping (X)—CH(Y)—CH_2—(Z) (where X, Y, Z introduce no further coupling). Only 6 lines out of the theoretical 8 are apparent in the AB region, but this is because of overlap of lines 2 and 5, and of

[7] N. S. Bhacca L. Johnson and J. Shoolery *Nuclear Magnetic Resonance Spectra Catalog*, Spectra Nos. 305, 306. Varian Associates, Palo Alto (1962).

[8] L. M. Jackman, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, [a] p. 126; [b] p. 55; [c] pp. 52–53; [d] p. 58. Pergamon Press, London (1959).

[9] J. A. Pople W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* pp. 132–138. McGraw-Hill, New York (1959).

4 and 7. This must be the case because of several conditions which the AB part of the ABX spectrum must satisfy—spacings 5,6 and 7,8 are equal; spacings 1,3 and 2,4 and 5,7 and 6,8 are equal to one another, giving J_{AB}. Further, the separation between lines 9 and 12 in the X part of the spectrum must be $(J_{AX} + J_{BX})$, and the separation between the centres of the two quartets in the AB part is $\frac{1}{2}(J_{AX} + J_{BX})$. Also the spacings 1,5 and 3,7 must be equal (giving 2D+) and spacings 2,6 and 4,8 must be equal (giving 2D−). It has been found that $J_{AB} = 5$ c/s directly, and by calculation that $J_{BX} = 1{\cdot}56$ c/s and $J_{AX} = 16{\cdot}45$ c/s. As the coupling between geminal protons lies in the range 12–20 c/s, it is concluded that the A and B protons must be vicinal,



with A and X geminal (CH_B—C). It is unusual for geminal protons to have different chemical shifts, although some examples are known in the cyclopropane series. Thus Wiberg and Nist[10] found in 1-phenyl-1,3-cyclopropanedicarboxylic acid that the chemical shifts of $H_a = 7{\cdot}63$, $H_b = 7{\cdot}92$, and $H_c = 8{\cdot}44$, so that $\Delta(H_c - H_b)$ is larger than the chemical shift between protons a and b on different carbon atoms.

Consideration of the chemical shifts leads to a rejection of structure (B). The chemical shift for CH_2—O·R is 6·60.[8b] A five-membered ring, phenyl group, and C=C bond will cause paramagnetic shifts of 0·25, 0·35 and 0·05 ppm,[8c] respectively, so that a predicted value for the CH_2 group resonance in (B) would be τ 5·95. It is not possible for the other substituents (B) to raise the value to that observed (ca. 7·6).

Structure (C) appears to be consistent with the chemical shifts. The CH proton in the grouping Ph·CH has τ 7·13.[8d] The five-membered ring and adjacent double bond will cause paramagnetic shifts of 0·25 and 0·15 ppm.[8c] Hence a predicted value for the CH group in (C) is r 6·73. The CH_2 group is in a five-membered ring, β to two phenyl groups and to a double bond. Hence a predicted line position[8c] is 8·75 − (0·25 + 0·7 + 0·05) = τ 7·75, and this might well be lowered by the third phenyl group which is not far away in space. However, it seems possible for the geminal protons (i.e. those of the CH_2 group) in (C) to have very different chemical shifts, as the spectrum analysis demands. Hence (C) must be rejected.

Structure IVb fits the observations and has an ABX system.[10]

The assignment of structure IVb is supported by its IR spectrum which exhibits strong absorption for the C=O and C=N groups. The spectrum of IVa similarly shows absorption characteristic of the carbonyl and C=N groups, but absence of NH absorption; thus favouring the "N-methylation" with diazomethane. This is in contrast to the IR spectrum of IIIa which shows characteristic absorption for the imide I and II.

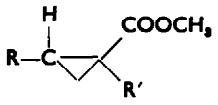
Cyclopropane ring formation (cf. IVc) has been reported upon treatment of IIIc with ethereal diazomethane.[11] With methanol, ring opening reactions accompanied with cyclopropane ring formation, have been reported in the case of Va[12] and Vb.[13]

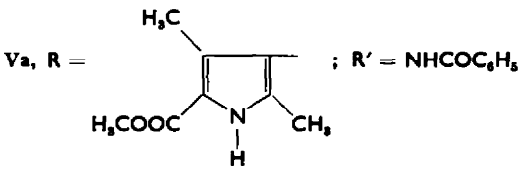
[10] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.* **85**, 2788 (1963).

[11] H. T. Clarke, J. R. Johnson and R. Robinson, *The Chemistry of Penicillin* p. 736. Princeton Univ. Press, New York (1949).

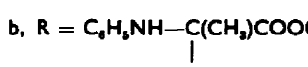
[12] H. Fischer and H. J. Hofman, *Z. physiol. Chem.* (Hoppe-Seyler's) **245**, 139 (1937).

[13] Th. Wieland and R. K. Rothhaupt, *Chem. Ber.* **89**, 1179 (1956).





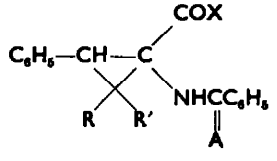
Va, R = ; R′ = $NHCOC_6H_5$



b, R = C_6H_5NH—C(CH_3)$COOCH_3$; R′ = OH.

Whereas "C-methylation" of IIId to IIIe, probably via an unstable pyrazoline, is effected by the action of ethereal diazomethane, cyclopropane formation (cf. IVd) takes place upon treatment of IIIe with the same reagent. In analogy to IIIc, IIIf and the sulphur analogues of IIIc, namely, IIIi and IIIj, react with the same reagent to give colourless cyclopropane derivatives (IVe and IVi–j), respectively.

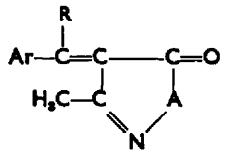
The ring-opening reactions of thiazolones are analogous to those of the oxazolones.[14] By the action of alcoholic potassium hydroxide on IVi, the corresponding acid (VIa) has been obtained; the latter cyclizes readily to IVi upon refluxing with acetic anhydride. Moreover, VIa with ethanolic silver nitrate[14] gave VIb which has been proved to be identical with the product obtained by the action of alcoholic potassium hydroxide on IVc. Opening of the thiazolidine ring in IVi has also been effected by the action of ammonia and/or aniline to yield VIc–d, respectively. The latter compounds are readily transformed, upon treatment with ethanolic silver nitrate, to the corresponding oxygen–analogues (VIe–f), which are obtained, as well, by the action of the same reagents on IVc.



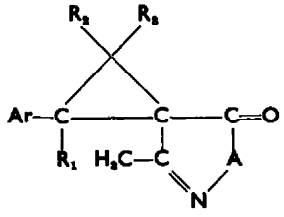
VIa, R = R′ = H; X = OH; A = S
b, R = R′ = H; X = OH; A = O
c, R = R′ = H; X = NH_2; A = S
d, R = R′ = H; X = NHC_6H_5; A = S
e, R = R′ = H; X = NH_2; A = O
f, R = R′ = H; X = NHC_6H_5; A = O
g, R and R′ = $C_{12}H_8$; X = OH; A = O

Treatment of the highly coloured compounds (VIIa–c) with diazomethane yield colourless cyclopropane derivatives (VIIIa–c). That the reaction product, VIIIb, is not identical with the coloured 4-(β-m-nitrophenyl-β-methylvinylidene)-3-methyl-1-phenyl-5-pyrazolone, now obtained by the condensation of 3-methyl-1-phenyl-5-pyrazolone with *m*-nitroacetophenone, excludes the possibility of "C-methylation",[4] and is taken in favour of the proposed cyclopropane structure.

[14] J. B. Jepson, A. Lawson and V. D. Lawton, *J. Chem. Soc.* 1791 (1955).



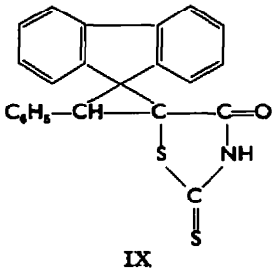
VIIa, Ar = C_6H_4Cl-o; R = H; A = NC_6H_5
b, Ar = $C_6H_4NO_2$-m; R = H; A = NC_6H_5
c, Ar = R = C_6H_5; A = NC_6H_5
d, Ar = $C_6H_4OCH_3$-p; R = H; A = NC_6H_5
e, Ar = C_6H_5; R = H; A = O
f, Ar = $C_6H_4CH_3$-p; R = H; A = O



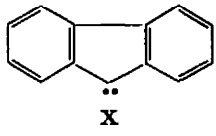
VIIIa, Ar = C_6H_4Cl-o; $R_1 = R_2 = R_3$ = H; A = NC_6H_5
b, Ar = $C_6H_4NO_2$-m; $R_1 = R_2 = R_3$ = H; A = NC_6H_5
c, Ar = $R_1 = C_6H_5$; $R_2 = R_3$ = H; A = NC_6H_5
d, Ar = C_6H_4Cl-o; R_1 = H; R_2 and $R_3 = C_{12}H_8$; A = NC_6H_5
e, Ar = $C_6H_4OCH_3$-p; R_1 = H; R_2 and $R_3 = C_{12}H_8$; A = NC_6H_5
f, Ar = C_6H_5; R_1 = H; R_2 and $R_3 = C_{12}H_8$; A = O
g, Ar = $C_6H_4CH_3$-p; R_1 = H; R_2 and $R_3 = C_{12}H_8$; A = O

It is well established that cyclopropane formation accompanies the action of 9-diazofluorene on unsaturated compounds.[15]

We now have found that when the coloured IIIc, g–h, VIIa,d, VIIe–f and Ic react with 9-diazofluorene in boiling benzene yielding IVf–h, IVk, VIIId–e, VIIIf–g and IX, respectively.



IX



X

The proposed cyclopropane structure finds analogy with the known addition reactions of 9-diazofluorene to unsaturated compounds,[15] and these reactions may involve combination of the carbene (X) with the conjugated olefins.[15h] The hetero-ring in IVf is opened to yield VIg by the action of hydrochloric acid.

[15a] A. Schönberg, A. Mustafa and N. Latif, *J. Amer. Chem. Soc.* **75**, 2267 (1953); [b] A. Mustafa and A. H. E. Harhash, *Ibid.* **76**, 1383 (1954); [c] L. Horner and E. Lingnau, *Liebigs Ann.* **573**, 30 (1951); [d] H. Staudinger and A. Gaule, *Ber. Dtsch. Chem. Ges.* **49**, 1956 (1916); [e] A. Mustafa and A. H. E. Harhash, *J. Amer. Chem. Soc.* **78**, 1649 (1956); [f] A. Mustafa, S. M. A. D. Zayed and S. A. Khattab, *Ibid.* **78**, 145 (1956); [g] A. Mustafa and M. Kamel, *Ibid.* **75**, 2939 (1953); [h] W. E. Parham, H. G. Brakston, Jr., and D. R. Theissen, *J. Org. Chem.* **27**, 2632 (1962).

The UV absorption spectra of VIIe and VIIIf are compatible with the proposed structure for the 9-diazofluorene product, VIIe absorps at 358 mμ with a very marked extinction coefficient (E: = 1553). This absorption is certainly compatible with a benzene ring conjugated with C=C bond which in turn is conjugated to C=O. This very significant band at 358 mμ disappears in VIIIf which only has the fluorene absorption; thus showing that the conjugation has been interrupted. The IR spectra of both VIIe and VIIIf contain a broad band in the carbonyl region which may be associated with a carbonyl group in a five-membered ring. The IR spectra of both compounds do not show any OH or NH absorption, but VIIe shows a small sharp band at 6·2 μ which should be associated to C=C bond. The proposed configuration, VIIIf, contains a highly substituted cyclopropane ring. The IR data tentatively support this structure. Derfer *et al.*[16] have shown that a breathing vibration of the three-membered ring occurs characteristically between 1020 to 1000 cm^{-1}. Normally this band is relatively intense; however, heavy substitution may weaken the intensity considerably, as in the case of 1,1,2,2-tetramethylcyclopropane. A weak band does occur in the spectrum of VIIIf at 1013 cm^{-1}. The assignment of this band to the cyclopropane system is only tentative. The occurrence of absorption cannot be accepted as definite evidence, whereas, the absence of a band may well be considered as proof against the presence of the cyclopropane ring.[15a]

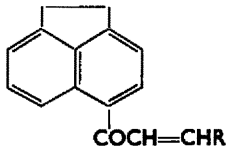
The IR spectra of IVf, IVk, VIIId and IX show characteristic absorption in the carbonyl region, and imide I and II in the case of IX.

In this connection, we would like to report the reaction of a number of newly prepared chalkones with diazomethane[17] and proof of the structure of the resulting pyrazolines.

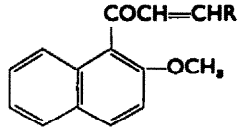
The chalkones XIa–f and XIIa,c–j were treated with an excess of diazomethane under comparable conditions, with the formation of the corresponding pyrazolines (XIIIa–e) and (XIVa–i), respectively. In the case of XIII, methylation of the OH group as well as addition to the α,β-unsaturated C=C bond took place to form the pyrazoline derivative, XIVd. On the other hand, treatment of XIIm–n with ethereal diazomethane solution under normal conditions effected only addition of the reagent to the C=C bond with the formation of the pyrazolines XIVj–k, respectively. The latter result may find parallelism with the emphasis reported recently by Ralls[18] and Geissman[19] in using alcohol-free diazomethane to avoid possible reaction of a lactam portion of a compound having other functional groups which would react preferentially, whereby, the reaction of lactams is promoted by alcohols. It seems possible that the α,β-unsaturated C=C bond in XIIm–n similarly reacts preferentially to the phenolic hydroxyl group in the presence of methanol-free diazomethane solution.

In contrast to the behaviour of *o*-hydroxychalkones toward the action of ethereal-diazomethane in presence of methanol, the benzylidene derivative of 2-hydroxy-1-acetylnaphthalene is recovered upon treatment with the same reagent in presence or absence of methanol under the reported conditions. The reaction of diazomethane

[16] J. M. Derfer, E. E. Pickett and C. E. Boord, *J. Amer. Chem. Soc.* **71**, 2482 (1949); cf. also R. A. Moss, *J. Org. Chem.* **27**, 2683 (1962).
[17] Cf. A. Mustafa and A. M. Fleifel, *J. Org. Chem.* **24**, 1740 (1959).
[18] J. W. Ralls, *J. Org. Chem.* **26**, 66 (1961).
[19] T. A. Geissman and A. K. Cho, *J. Org. Chem.* **24**, 41 (1959).

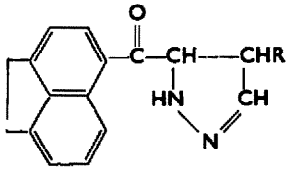


XIa, R = C_6H_5
b, R = C_6H_4Cl-*o*
c, R = C_6H_4Cl-*p*
d, R = C_6H_4OH-*m*
e, R = C_6H_4OH-*p*
f, R = $C_6H_4OCH_3$-*p*
g, R = C_6H_3:O_2:CH_2(3:4)
h, R = C_6H_4OH-*o*
i, R = $C_6H_4OCH_3$-*o*
j, R = $C_6H_4OC_2H_5$-*o*
k, R = $C_6H_4NO_2$-*m*.

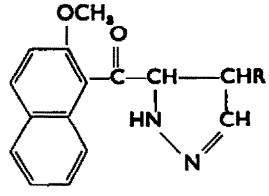


XIIa, R = C_6H_5
b, R = $C_6H_4CH_3$-*m*
c, R = $C_6H_4CH_3$-*p*
d, R = $C_6H_4OCH_3$-*o*
e, R = $C_6H_4OCH_3$-*p*
f, R = C_6H_3:O_2:CH_2(3:4)
g, R = $C_6H_3(OCH_3)_3$(3:4)
h, R = C_6H_4Cl-*o*
i, R = $C_6H_4NO_2$-*o*
j, R = $C_6H_4NO_2$-*m*
k, R = $C_6H_4NO_2$-*p*
l, R = C_6H_4OH-*p*
m, R = C_6H_4OH-*o*
n, R = C_6H_3OH·Cl(2:5).

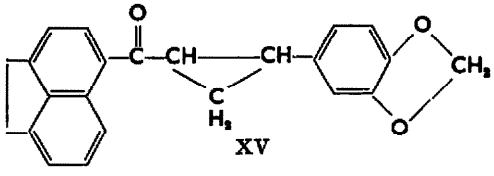
with XIg does not result in the formation of the corresponding pyrazoline, but immediately yields the cyclopropane derivative (XV).[2f,g,13,20]



XIIIa, R = C_6H_5
b, R = C_6H_4Cl-*o*
c, R = C_6H_4Cl-*p*
d, R = $C_6H_4OCH_3$-*m*
e, R = $C_6H_4OCH_3$-*p*



XIVa, R = C_6H_5
b, R = $C_6H_4CH_3$-*p*
c, R = $C_6H_4OCH_3$-*o*
d, R = $C_6H_4OCH_3$-*p*
e, R = C_6H_3:O_2:CH_2(3:4)
f, R = $C_6H_3(OCH_3)_3$(3:4)
g, R = C_6H_4Cl-*o*
h, R = $C_6H_4NO_2$-*o*
i, R = $C_6H_4NO_2$-*m*
j, R = C_6H_4OH-*o*
k, R = C_6H_3OH·Cl(2:5)
l, R = $C_6H_3OCH_3$·Cl(2:5).



XV

In view of the mechanism for the addition of diazomethane to α,β-unsaturated esters and ketones (cf. benzal-acetophenone), and the general acceptance that the methylene group becomes attached to the β-carbon atom,[2b,e,21] the addition products have the proposed pyrazoline structure. The IR absorption spectra of XIIIc and XIIIe, taken as examples, show absorption at 3340 cm^{-1} (—NH group) and absence of absorption near 1600 cm^{-1} (—N=N— group).[22] Moreover, the pyrazolines have been found to reduce permanganate in acetone at room temperature.[23] Thus showing

[20] P. C. Guha and S. Krischnamurthy, *Ber. Dtsch. Chem. Ges.* **70**, 2112 (1937).

[21a] von K. Auwers and E. Cauer, *Liebigs Ann.* **470**, 284 (1920); [b] von K. Auwers and O. Ungemach, *Ber. Dtsch. Chem. Ges.* **66**, 1206 (1933); [c] L. I. Smith and W. B. Pings, *J. Org. Chem.* **2**, 23 (1937); L. I. Smith and K. L. Howard, *J. Amer. Chem. Soc.* **65**, 159 (1943).

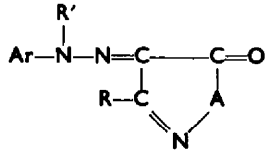
[22] W. E. Parham, F. D. Blake and D. R. Theissen, *J. Org. Chem.* **27**, 2415 (1962).

[23] F. B. Baltzly, N. B. Mehta, P. B. Russel, R. E. Brooks, E. M. Grivsky and A. M. Steinberg, *J. Org. Chem.* **26**, 3669 (1961); *Ibid.* **27**, 213 (1962).

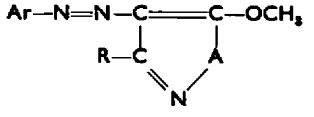
that the position of the double bond can be placed with more certainty and the pyrazolines are Δ^2-pyrazolines or their possible tautomers.[24]

Treatment of XVIa with ethereal diazomethane yields XVIf together with XVIIa.

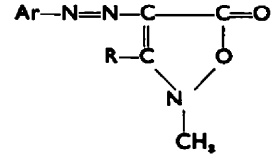
The assignment of structure XVIf finds analogy with XVIg proposed by Meyer[25] for the product obtained by the action of diazomethane on XVIb. Moreover, the IR spectrum of XVIf shows a strong carbonyl as well as C=N absorption. Structure XVIIa finds support from its IR absorption which reveals the absence of characteristic frequency in the carbonyl region and the exhibition of absorption around 1600 cm^{-1} (—N=N— group).[22] Moreover, it has been found that XVIIa is not identical with XVIIIa, now obtained either by the action of dimethyl sulphate on XVIa,[26] or by the condensation of N-methylhydroxylamine with ethyl α-*p*-tolylazoacetoacetate in alcohol. The heterocyclic ring in XVIIIa is readily cleaved by the action of hot acetic acid with the formation of α-*p*-tolylazoacetoacetic acid; the latter is also obtained when the above condensation between N-methylhydroxylamine and ethyl α-*p*-tolylazoacetoacetate was carried out using acetic acid instead of alcohol. Similar cleavage can be brought about when XVIIIa was treated with phenylhydrazine in the presence of acetic acid, yielding 3-methyl-1-phenyl-4-*p*-tolylazo-5-pyrazolone. Alkaline reduction cleavage of the exocyclic *p*-tolylazo group in XVIIa and XVIIIa resulted in the formation of *p*-toluidine.



XVIa, R = CH_3; R′ = H; Ar = $C_6H_4CH_3$-*p*; A = O (or tautomer)
b, R = Ar = C_6H_5; R′ = H; A = O (or tautomer)
c, R = C_6H_5; R′ = H; Ar = $C_6H_4CH_3$-*o*; A = O (or tautomer)
d, R = C_6H_5; R′ = H; Ar = $C_6H_4CH_3$-*p*; A = O (or tautomer)
e, R = CH_3; R′ = H; Ar = C_6H_5; A = NC_6H_5 (or tautomer)
f, R = R′ = CH_3; Ar = $C_6H_4CH_3$-*p*; A = O
g, R = Ar = C_6H_5; R′ = CH_3; A = O
h, R = C_6H_5; R′ = CH_3; Ar = $C_6H_4CH_3$-*o*; A = O
i, R = C_6H_5; R′ = CH_3; Ar = $C_6H_4CH_3$-*p*; A = O
j, R = R′ = CH_3; Ar = C_6H_5; A = NC_6H_5



XVIIa, R = CH_3; Ar = $C_6H_4CH_3$-*p*; A = O
b, R = Ar = C_6H_5; A = O
c, R = C_6H_5; Ar = $C_6H_4CH_3$-*o*; A = O
d, R = C_6H_5; Ar = $C_6H_4CH_3$-*p*; A = O
e, R = CH_3; Ar = C_6H_5; A = NC_6H_5



XVIIIa, R = CH_3; Ar = $C_6H_4CH_3$-*p*
b, R = Ar = C_6H_5

Structure XVIIb, now proposed for the unidentified product described by Meyer,[25] finds support from its IR spectrum which reveals the absence of absorption in the

[24] Cf. also the ready rearrangement of Δ^1-pyrazolines to Δ^2-pyrazolines by repeated crystallisation or even by the effect of the glassware, Ref. 2b, 21c.

[25] A. Meyer, *Ann. Chimie et Phys.* "9" **1**, 302 (1914).

[26] Cf. A. Michaelis and H. Schlect, *Ber. Dtsch. Chem. Ges.* **39**, 1954 (1906).

carbonyl region and the presence of absorption around 1600 cm^{-1} (—N=N— group). Moreover, it has been shown not to be identical with XVIIIb, now obtained by the action of dimethyl sulphate on XVIb. Similarly, treatment of XVIc–d with ethereal diazomethane resulted in a mixture of the N-methylhydrazono derivatives (XVIh–i), and the O-methyl derivatives (XVIIc–d), respectively.

3-Methyl-1-phenyl-4-phenylazo-5-pyrazolone may have the structure shown in XVIe or one of its possible tautomeric forms. Auwers and Boennecke[27] reported the formation of XVIj upon methylation of XVIe with methyl iodide in presence of sodium methylate, and the formation of XVIj together with XVIIe with dimethyl sulphate.

TABLE 2. LIST OF NEW CHALKONES[a]

Chalkone	Solvent[b] for cryst.	M.p.	Yield %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.
XIa	A	104°	70	$C_{21}H_{16}O$	88·34	88·73	5·85	5·63
XIb	A	113°	65	$C_{21}H_{15}OCl$[c]	79·52	79·12	4·90	4·71
XIc	A	150°	72	$C_{21}H_{15}OCl$[d]	78·79	79·12	4·81	4·71
XId	A	159°	70	$C_{21}H_{16}O_2$	83·46	84·00	5·34	5·33
XIe	A	173°	75	$C_{21}H_{16}O_2$	83·47	84·00	5·51	5·33
XIf	A	110°	80	$C_{22}H_{18}O_2$	83·82	84·08	5·72	5·73
XIg	A	162°	75	$C_{22}H_{18}O_2$	80·63	80·48	5·09	4·88
XIh	A	159°	70	$C_{21}H_{16}O_2$	84·05	84·00	5·39	5·33
XIi	A	133°	65	$C_{22}H_{18}O_2$	83·81	84·08	5·82	5·73
XIj	A	98°	70	$C_{23}H_{20}O_2$	83·65	84·15	6·06	6·09
XIk	A	188°	60	$C_{21}H_{15}O_2N$[e]	76·90	76·59	4·68	4·56
XIIa	A	140°	80	$C_{20}H_{16}O_2$	82·95	83·33	5·35	5·55
XIIb	B	80°	60	$C_{21}H_{18}O_2$	83·44	83·43	6·20	5·96
XIIc	A	76°	90	$C_{21}H_{18}O_2$	83·82	83·43	5·85	5·96
XIId	A	127°	95	$C_{21}H_{18}O_2$	79·16	79·24	5·61	5·66
XIIe	A	112°	95	$C_{21}H_{18}O_2$	79·30	79·24	5·85	5·66
XIIf	A	134°	95	$C_{21}H_{16}O_4$	75·50	75·90	4·60	4·82
XIIg	A	131°	93	$C_{22}H_{20}O_4$	75·75	75·86	5·64	5·74
XIIh	A	138°	50	$C_{20}H_{15}O_2Cl$[f]	74·80	74·41	4·50	4·65
XIIi	B	130°	70	$C_{20}H_{15}O_4N$[g]	72·56	72·07	4·32	4·50
XIIj	B	105°	80	$C_{20}H_{15}O_4N$[h]	72·05	72·07	4·54	4·50
XIIk	B	165°	62	$C_{20}H_{15}O_4N$[i]	71·75	72·07	4·33	4·50
XIIl	B	170°	60	$C_{20}H_{16}O_2$	78·87	78·94	5·33	5·26
XIIm	A	146°	90	$C_{20}H_{16}O_2$	78·60	78·94	5·07	5·26
XIIn	A	187°	85	$C_{20}H_{15}O_2Cl$[j]	70·60	70·90	4·60	4·43

[a] Prepared after the procedure described by Mustafa and Fleifel, Ref. 17.
[b] A, Ethanol; B, Benzene–pet. ether (b.p. 70–80°).
[c] Cl, Found, 11·07; Calc. 11·14.
[d] Cl, Found, 11·07; Calc. 11·14.
[e] Cl, Found, 11·30; Calc. 11·00.
[f] N, Found, 4·47; Calc. 4·25.
[g] N, Found, 4·42; Calc. 4·20.
[h] N, Found, 4·30; Calc. 4·20.
[i] N, Found, 4·40; Calc. 4·20.
[j] Cl, Found, 10·70; Calc. 10·48.

[27] von K. Auwers and A. Boennecke, *Liebigs Ann.* 378, 218 (1911).

TABLE 3. LIST OF CYCLOPROPANES

Compound used	Product	Solvent[a] for cryst.	M.p.	Yield, %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found	Nitrogen, % Calc.	Sulphur, % Found	Sulphur, % Calc.
IIIa	IVa	A	225°	65	$C_{15}H_{16}ON_2$	78·01	78·26	5·54	5·79	10·30	10·01		
IIIb	IVb	B	162°	65	$C_{22}H_{18}ON_2$	81·33	81·65	5·22	5·32	8·07	8·28		
IIIe[b]	IVb	C	58°	60	$C_{13}H_{13}O_2N$	72·36	72·55	6·18	6·05	6·42	6·51		
IIIf	IVe	D	162°	70	$C_{21}H_{15}O_2N$	80·25	80·51	4·68	4·79	4·36	4·47		
IIIc	IVf	D	189°	70	$C_{28}H_{19}O_2N$	84·15	84·26	4·45	4·60	3·06	3·37		
IIIg	IVg	D	209°	80	$C_{30}H_{21}O_2N$	81·03	81·26	4·53	4·74	3·00	3·16		
IIIh	IVh	D	211°	75	$C_{30}H_{19}O_4N$	78·47	78·77	3·94	4·15	2·85	3·06		
IIIi	IVi	E	125°	75	$C_{17}H_{13}ONS$	73·01	73·15	6·07	6·37	6·74	6·86	15·38	15·68
IIIj[c]	IVj	B	134°	70	$C_{17}H_{12}ONSCl$[d]	64·86	65·07	3·74	3·82	4·32	4·46	11·06	11·24
IIIj	IVk	G	183°	65	$C_{31}H_{18}ONSCl$[e]	75·24	75·08	3·61	3·88	3·14	3·02	6·75	6·90
VIIa	VIIIa	F	149°	70	$C_{16}H_{15}ON_2Cl$[f]	69·51	69·56	4·81	4·83	9·00	9·02		
VIIb	VIIIb	F	191°	65	$C_{15}H_{15}O_3N_3$	67·29	67·24	4·63	4·67	13·00	13·08		
VIIc	VIIIc	F	108°	80	$C_{24}H_{20}ON_2$	81·79	81·82	5·65	5·68	7·92	7·95		
VIIa	VIIId	F	162°	70	$C_{30}H_{21}ON_2Cl$[g]	78·11	78·17	4·51	4·56	6·00	6·08		
VIId	VIIIe	D	170°	75	$C_{31}H_{24}O_3N_2$	81·55	81·58	5·19	5·26	6·11	6·14		
VIIe	VIIIf	D	154°	65	$C_{24}H_{17}O_2N$	81·72	82·05	4·65	4·84	3·73	3·98		
VIIf	VIIIg	D	175°	75	$C_{28}H_{19}O_2N$	82·41	82·19	5·06	5·20	3·52	3·83		
Ic	IX	D	192°	60	$C_{22}H_{15}ONS_2$	71·39	71·66	3·58	3·89	3·43	3·63	16·44	16·59
XIg	XV	D	165°	75	$C_{23}H_{18}O_2$	80·52	80·70	5·06	5·20				
XVIa	XVIId	D	181°	65	$C_{26}H_{18}O_2NSCl$[h]	70·05	70·34	4·11	4·06	3·01	3·15	7·18	7·21
XVIb	XVIIe	H	239°	70	$C_{28}H_{19}O_4N_2S$	68·52	68·72	3·74	3·96	5·84	6·16	6·99	7·05

[a] A, Acetone; B, Benzene–pet. ether (b.p. 60–80°); C, Dilute alcohol; D, Benzene; E, Petroleum ether b.p. (60–80°); F, Ethanol; G, Acetic acid; H, Xylene.

[b] Obtained in 55% yield by the action of diazomethane on IIId and is identical with a specimen prepared after Ramage and Simonsen (G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.* 534 (1935)).

[c] Prepared after the procedure described by Filler and Rao (R. Filler and Y. S. Rao, *J. Org. Chem.* **27**, 3730 (1962)) as pale yellow crystals from ethanol–benzene, m.p. 194° (yield, 80%). (Found: C, 63·84; H, 3·14; N, 4·56; S, 10·33; Cl, 11·58. $C_{16}H_{10}$ ONSCl requires: C, 64·17; H, 3·34; N, 4·67; S, 10·68; Cl, 11·85%.)

[d] Cl, Found, 11·37; Calc., 11·32.

[e] Cl, Found, 7·53; Calc., 7·65.

[f] Cl, Found, 11·39; Calc., 11·11.

[g] Cl, Found, 7·62; Calc., 7·71.

[h] Cl, Found, 7·85; Calc., 8·00.

Structure XVIIe now has been rigorously proved by the fact that it is not identical with 3,4-dimethyl-1-phenyl-4-phenylazo-5-pyrazolone, recently described by Pelz *et al.*[28] via interaction of 3,4-dimethyl-1-phenyl-5-pyrazolone with benzenediazonium chloride, and its identity with an authentic specimen, now obtained by the action of sodium methylate on 5-chloro-3-methyl-1-phenyl-4-phenylazopyrazole. Moreover, the IR spectrum for XVIIe reveals absorption around 1600 cm^{-1} (—N=N— group) but absence of absorption in the carbonyl region.

In our hands the action of ethereal diazomethane solution on XVIe leads to the formation of a mixture of XVIj and XVIIe.

EXPERIMENTAL[29,30,31]

Behaviour of IVc

(a) *With alcoholic potassium hydroxide.* A suspension of IVc[11] (0·5 g) in ethanolic KOH (10%, 50 ml) was refluxed for 1 hr, diluted with water, and acidified with dil. HCl. The acid (VIb), was crystallized from EtOH as colourless crystals, m.p. 244°, yield, 76%. (Found: C, 72·65; H, 5·12; N, 4·67. $C_{17}H_{16}O_3N$ requires: C, 72·60; H, 5·34; N, 4·98%.)

(b) *With ammonia.* A mixture of IVc (0·5 g), conc. NH_4OH (4·0 ml), and EtOH (50 ml) was refluxed for 30 min. The resulting solution was concentrated, and VIe, crystallized from EtOH as colourless crystals, m.p. 225°, yield, 63%. (Found: C, 72·63; H, 5·54; N, 9·87. $C_{17}H_{16}O_2N_2$ requires: C, 72·86; H, 5·71; N, 10·00%.)

(c) *With aniline.* A mixture of IVc (0·5 g) and aniline (2·0 ml) was heated at 180° (bath temp) for 15 min. The cooled reaction mixture was extracted with ether; the ethereal layer washed twice with cold dil. HCl, then with water, dried and evaporated. The solid anilide (VIf), was crystallized from EtOH as colourless crystals, m.p. 176°, yield, 57%. (Found: C, 77·16; H, 5·34; N, 7·65. $C_{23}H_{20}O_2N_2$ requires: C, 77·53; H, 5·62; N, 7·86%.)

Behaviour of IVi

(a) *With alcoholic potassium hydroxide.* Treatment of IVi with alcoholic KOH, as described above, yielded VIa, which crystallized from EtOH as pale yellow crystals, m.p. 180° (with dec), yield, 45%. (Found: C, 68·48; H, 4·92; N, 4·51; S, 10·45. $C_{17}H_{15}O_3NS$ requires: C, 68·69; H, 5·05; N, 4·71; S, 10·77%.)

When a solution of VIa (0·1 g) in acetic anhydride (5·0 ml) was refluxed for 15 min, followed by cooling, IVi separated out, yield, 86% (m.p. and mixed m.p.).

To a solution of VIa (0·1 g) in EtOH (50 ml), $AgNO_3$ aq (0·5 N, 10 ml) was added. The reaction mixture was refluxed 2 hr, filtered while hot from the separated Ag_2S, concentrated, and cooled. The colourless crystals proved to be VIb (m.p. and mixed m.p.), yield, 90%.

(b) *With ammonia.* Compound IVi (0·5 g) was treated with ammonia, as described above, and the VIc crystallized from benzene–pet. ether (b.p. 80–100°) as pale yellow crystals, m.p. 181° (with dec), yield, 52%. (Found: C, 68·74; H, 5·21; N, 9·32; S, 10·66. $C_{17}H_{16}ON_2S$ requires: C, 68·92; H, 5·41; N, 9·46; S, 10·81%.)

Treatment of VIc with alcoholic $AgNO_3$ afforded VIe (m.p. and mixed m.p.).

(c) *With aniline.* The anilide (VId), obtained via treatment of VIi with aniline was crystallized from EtOH as pale yellow crystals, m.p. 145°, yield, 64%. (Found: C, 73·99; H, 5·38; N, 7·44; S, 9·12. $C_{23}H_{20}ON_2S$ requires: C, 74·19; H, 5·38; N, 7·53; S, 8·60%.)

[28] W. Pelz, W. Peischel, H. Schellenberger and K. A. Loffer, *Angew. Chem.* 72, 967 (1960).

[29] Experiments with chalkones were carried out with A. M. Fleifel, M. A. Zowail and A. H. Lachine; imidazolones, 4-ethylidene-, 4-isopropylidene-, and 4-(1-naphthylidene)-5(4H)-oxazolones with M. M. Sallam and A. R. M. Elwi; thiazolones with E. M. Zayed; pyrazolones with A. F. A. M. Shalaby and Z. E. Selim; isoxazolones with A. H. Harhash, N. A. L. Kassab and A. K. Mansour.

[30] All m.ps are uncorrected. IR spectra were obtained, in Nujol, on a Perkin–Elmer Infracord, Model 137, and UV spectra were determined on a Peckman DK-2 spectrophotometer. NMR spectra were determined in $CDCl_3$ (~10%) containing 0·2% tetramethylsilane as internal standard.

[31] Reactions with diazomethane were carried out as described by Mustafa and Fleifel, Ref. 17; those with 9-diazofluorene after Mustafa and Harhash, Ref. 15*e*.

TABLE 4. LIST OF Δ^2-PYRAZOLINES

Compound used	Product	Solvent[a] for cryst.	M.p.	Yield, %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found	Nitrogen, % Calc.
XIa	XIIIa	A	204°	70	$C_{22}H_{18}ON_2$	80·73	80·98	5·45	5·52	8·86	8·59
XIb	XIIIb	A	173°	75	$C_{22}H_{17}ON_2Cl$[b]	73·63	73·23	4·55	4·71		
XIc	XIIIc	A	147°	70	$C_{22}H_{17}ON_2Cl$[c]	73·00	73·23	4·63	4·71		
XId	XIIId	A	164°	72	$C_{22}H_{20}O_2N_2$	77·20	77·53	5·64	5·62	8·16	7·86
XIe or XIf	XIIIe	A	161°	80	$C_{22}H_{20}O_2N_2$	76·93	77·53	5·63	5·62	8·06	7·86
XIIa	XIVa	B	171°	70	$C_{21}H_{16}O_2N_2$	76·65	76·36	5·33	5·45	8·63	8·48
XIIc	XIVb	C	160°	85	$C_{22}H_{20}O_2N_2$	76·84	76·74	5·81	5·81	8·13	8·13
XIId	XIVc[d]	C	116°	65	$C_{22}H_{20}O_3N_2$	72·96	73·33	5·25	5·55	7·69	7·77
XIIe or XIIl	XIVd	B	173°	75	$C_{22}H_{20}O_3N_2$	73·35	73·33	5·12	5·55	7·74	7·77
XIIf	XIVe	C	192°	80	$C_{22}H_{16}O_4N_2$	70·65	70·59	4·91	4·81	7·38	7·48
XIIg	XIVf	B	174°	75	$C_{22}H_{22}O_4N_2$	70·50	70·76	5·36	5·64	7·20	7·18
XIIh	XIVg	C	219°	70	$C_{21}H_{17}O_2N_2Cl$	69·30	69·13	4·93	4·66	7·48	7·68
XIIi	XIVh	B	227°	55	$C_{21}H_{17}O_4N_3$	67·04	67·20	4·20	4·54	11·25	11·20
XIIj	XIVi	B	177°	70	$C_{21}H_{17}O_4N_3$	67·37	67·20	4·21	4·54	11·41	11·20
XIIm	XIVj	C	90°	60	$C_{21}H_{18}O_3N_2$	72·91	72·85	5·31	5·20	7·90	8·09
XIIn	XIVk	B	213°	60	$C_{21}H_{17}O_2N_3Cl$	66·30	66·22	4·70	4·46	7·37	7·35
XIIn	XIVl[e]	C	115°	65	$C_{22}H_{19}O_3N_2Cl$	66·54	66·92	4·65	4·81	7·20	7·09

[a] A, Benzene; B, ethanol; C, benzene–pet. ether (b.p. 50–70°).
[b] Cl, Found, 9·20; calc. 9·87.
[c] Cl, Found, 9·62; calc., 9·87.
[d] Can also be obtained by the action of methanol-containing diazomethane on XIIm.
[e] The reaction was carried out in the presence of methanol.

TABLE 5. PRODUCTS OF ARYLAZO COMPOUNDS WITH DIAZOMETHANE

Arylazo derivative	Product[a]	M.p.	Yield, %	Formula	Carbon, % Found	Carbon, % Calc.	Hydrogen, % Found	Hydrogen, % Calc.	Nitrogen, % Found.	Nitrogen, % Calc.
XVIa	XVIf	157°	43	$C_{12}H_{12}O_2N_2$	62·11	62·34	5·42	5·63	17·89	18·18
	XVIIa[b]	101°	35	$C_{12}H_{12}O_2N_2$	62·03	62·34	5·52	5·63	18·01	18·18
XVIb	XVIg	148°	45	$C_{16}H_{12}O_2N_2$	68·71	68·82	4·43	4·66	14·81	15·05
	XVIIb	88°	31	$C_{16}H_{12}O_2N_2$	68·60	68·82	4·35	4·66	14·92	15·05
XVIc	XVIh	172°	46	$C_{17}H_{14}O_2N_2$	69·33	69·62	5·01	5·12	14·12	14·33
	XVIIc	95°	33	$C_{17}H_{14}O_2N_2$	69·41	69·62	4·81	5·12	14·23	14·33
XVId	XVIi	126°	41	$C_{17}H_{14}O_2N_2$	69·51	69·62	4·91	5·12	14·14	14·33
	XVIId	96°	35	$C_{17}H_{14}O_2N_2$	69·35	69·62	4·87	5·12	14·02	14·33
XVIe	XVIj[c]	144°	41							
	XVIIe[c,d]	78°	31							

[a] The ethereal reaction product was concentrated, cooled, the solid formed (higher m.p.) was filtered off; the mother liquor gave on evaporation the other product (lower m.p.). Both products were crystallized from alcohol.

[b] Reductive cleavage, after the procedure described by Auwers and Boennecke, Ref. 27, gave *p*-toluidine.

[c] Identical with a specimen prepared after Auwers and Boennecke, Ref. 27.

[d] Identical with an authentic specimen prepared in 55% yield by treatment of 5-chloro-3-methyl-1-phenyl-4-phenylazopyrazole with sodium methylate in methanol.

Similar treatment of VId with alcoholic $AgNO_3$, gave an almost quantitative yield of VIf (m.p. and mixed m.p.).

Action of acetic-hydrochloric acid mixture on IVf

A mixture of IVf (0·5 g), acetic acid (30 ml), and HCl (10 ml) was refluxed for 3 hr. The cooled reaction mixture was poured into ice-cold water; the solid (VIg), was crystallized from EtOH as colourless needles (0·34 g), m.p. 297°. (Found: C, 80·53; H, 4·61; N, 3·06. $C_{29}H_{21}O_3N$ requires: C, 80·74; H, 4·87; N, 3·25%.)

3-*Methyl*-1-*phenyl*-4-(*β*-m-*nitrophenyl*-*β*-*methylvinylidene*)-5-*pyrazolone*

A mixture of 3-methyl-1-phenyl-5-pyrazolone (0·1 mole), *m*-nitroacetophenone (0·1 mole), and fused sodium acetate (0·15 mole) was heated (oil-bath temp 115–120°) for 1 hr with continuous stirring. The red oily reaction mixture was cooled, poured onto ice, and the solid, crystallized from dil. acetic acid as yellow crystals, m.p. 92°, yield, 58%. (Found: C, 67·19; H, 4·70; N, 13·02. $C_{18}H_{15}O_3N_3$ requires: C, 67·29; H, 4·67; N, 13·09%.)

Action of dimethyl sulphate on XVIa–b

A suspension of XVIa (1 g) or XVIb (1 g) in dimethyl sulphate (10 ml) was refluxed for 10 min. The cooled reaction mixture was poured into ice-cold water, and the solid crystallized from EtOH.

Compound XVIIIa formed deep yellow needles, m.p. 185°, yield, 64%. (Found: C, 62·57; H, 5·80; N, 18·35. $C_{12}H_{12}O_2N_2$ requires: C, 62·34; H, 5·63; N, 18·18%.) Reductive cleavage[27] of XVIIIa effected the isolation of *p*-toluidine.

Compound XVIIIa was proved to be identical with the product, obtained in 72% yield upon refluxing a mixture of ethyl α-p-tolylazoacetoacetate (1·0 g), N-methylhydroxylamine hydrochloride (1·5 g), sodium acetate (1·5 g), and EtOH (50 ml) for 2 hr. Identification was carried out by m.p. and mixed m.p. determinations.

When in the above condensation reaction, acetic acid was used instead of EtOH, α-*p*-tolylazoacetic acid was obtained in 65% yield (m.p. and mixed m.p.). Moreover, refluxing a suspension of XVIIIa (0·5 g) in acetic acid (30 ml) for 1 hr, resulted in 76% yield of α-*p*-tolylazoacetic acid.

Treatment of XVIIIa (0·5 g) with a solution of phenylhydrazine (1·0 ml) in acetic acid (50 ml)

and refluxing the reaction mixture for 30 min, followed by pouring into ice-cold water, effected the formation of 3-methyl-1-phenyl-4-*p*-tolylazo-5-pyrazoline (0·32 g) (m.p. and mixed m.p.).

Compound XVIIIb gave orange needles, m.p. 221°, yield, 68%. (Found: C, 68·60; H, 4·41; N, 14·84. $C_{16}H_{12}O_3N_2$ requires: C, 68·82; H, 4·66; N, 15·05%.)

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