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REACTIONS OF SOME DIAZOAZOLES WITH REACTIVE METHYLENE AND OTHER GROUPS[1]

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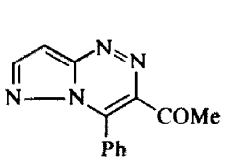
Abstract—Reactions of some heteroaromatic diazo compounds with 1,3-dicarbonyl compounds, amines and thiophenol to give bi- and tricyclic heterocycles are studied. Decomposition of heterocyclic diazo compounds, triazenes and related compounds are investigated.

Heterocyclic diazo compounds represent an interesting class of reactive substrates and their stability depends mainly on charge delocalization through the heterocyclic ring. Recently we have described the reaction between 3-diazo-(3*H*)indazole and reactive methylene compounds and the formation of indazolo(3,2-*c*)-1,2,4-triazines and related systems. We now report similar reactions of 5-carboxamido-4-diazoimidazole, pyrazole-3-diazonium chloride and 3-diazo-(3*H*)indazole.

Because of the reported instability of 3-diazopyrazole[3] reactions have been carried out with pyrazole-3-diazonium chloride. The latter reacted at room temperature with β-keto esters to give derivatives of pyrazolo-(5,1-*c*)-1,2,4-triazine. Some representatives of this system have been reported earlier.[4] From the reaction with benzoyl-acetone two isomeric products can be formed, a 3-acetyl-4-phenyl derivative **1** or a 3-benzoyl-4-methyl derivative. We established that only one product was formed in the above reaction and through NMR data the structure **1** was assigned. In a similar manner 1,3-cyclohexanedione or its 5,5-dimethyl derivative reacted to give the corresponding pyrazolo-(5,1-*c*)-1,2,4-benzotriazinones **2**. In contrast to the dimethyl derivative (**2**; R = Me) the unsubstituted tricyclic compound (**2**; R = H), after being heated *in vacuo* at 150°, was aromatized and transformed into **3**.

The intermediate coupling products were isolated in the case of diazoindazole,[2] but no such intermediates could be isolated in the above-mentioned reactions. This is understandable if we take into account that the diazonium salt was used and that the generated acid acted as catalyst for the cyclization step. An exception was the coupling product with 1,3-indanedione, which reacted with pyrazole-3-diazonium chloride to give a mixture of **4** and **5**. Both compounds are interconvertible, thermal cyclization of **4** gives compound **5** and this is transformed back into **4** with alkali. 2-Carbethoxycyclopentanone reacted in a different way to give the open chain compound **6**, the reaction being an example of the Japp-Klingemann reaction.[5] Thermal cyclization of **6** afforded the pyrazolo-(5,1-*c*)-1,2,4-triazine derivative **7**.

Further experiments were performed with the relatively unstable 5-carboxamido-4-diazoimidazole which may cyclize easily into imidazo - (4,5 - *d*) - v - triazin - 4(3*H*) - one (2-azahypoxanthine), particularly in solution.[6] The formation of this compound competes with the coupling reaction with 1,3-dicarbonyl compounds. The coupling products **8** could be obtained when an ethanolic solution of the diazo-compound and the 1,3-dicarbonyl compound was left to stand at room temperature. Again, the Japp-Klingemann reaction took place in the case of 2-carbethoxy-cyclopentanone or cyclohexanone to give **8f** and **8g**. The open chain compounds **8** could not be transformed into the cyclic imidazo(1,5 - *c*) - 1,2,4 - triazines **9** by acid catalyzed cyclization. A spectroscopic examination of the products revealed that they contained some cyclic products in admixture with **8**. However, if the reaction mixture of **8c** was treated at the end of the reaction with alkali, compound **10** could be obtained. The structure of the later follows from spectral data and mass spectral fragmentation ($m/e = 105$ corresponds to the PhCO fragment). Another example of the Japp-Klingemann reaction was observed with benzoylacetic acid when coupling was followed by decarboxylation. The



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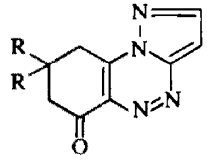

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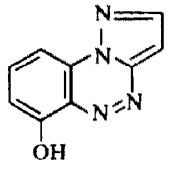

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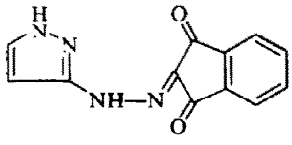

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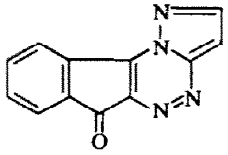

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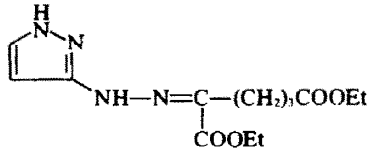

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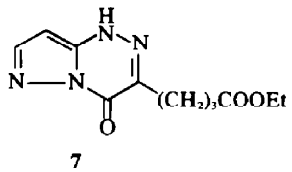

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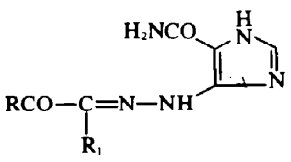

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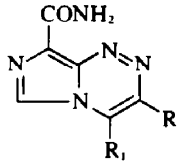

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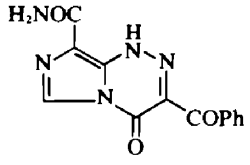
	R	R_1
a:	Me	COMe
b:	Me	COOEt
c:	Ph	COOEt
d:	CH_2COOEt	COOEt
e:	CN	COOEt
f:	OEt	$(CH_2)_4COOEt$
g:	OEt	$(CH_2)_3COOH$
h:	Ph	H



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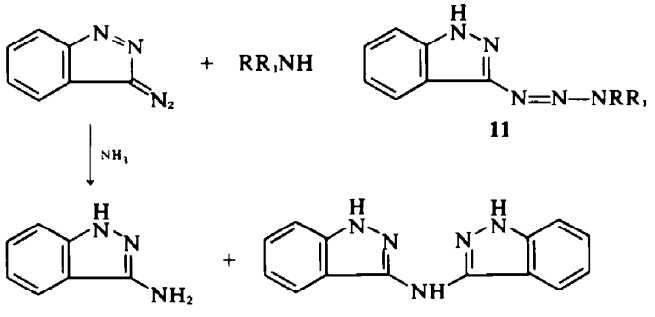
product **8h** should be the same as that of anticipated coupling to acetophenone which proved to be unsuccessful.

Thiophenol reacted to form the corresponding diazosulphide **13**. This was thermally decomposed into a mixture of indazole, diphenyl sulphide and 3-indazolyl



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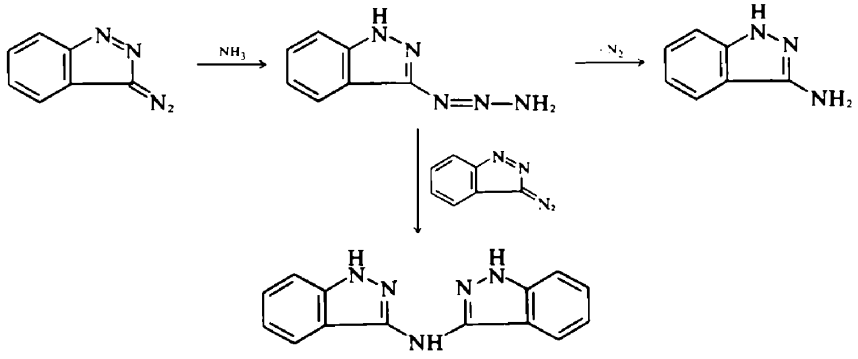
12

	R	R_1
a:	H	Et
b:	Et	Et
c:	i-Pr	i-Pr
d:	H	Ph
e:	H	pyridyl-2
f:	H	indazolyl-3

Although pyrazole-3-diazonium chloride and 5-carboxamido-4-diazoimidazole reacted with amines to form triazenes, these could not be isolated pure. However, the benzo analog of diazopyrazole, 3-diazo-(3*H*)indazole formed stable triazenes **11** with primary and secondary amines. It should be noted that the triazene **11e**, formed from 2-aminopyridine, is exceptionally stable since it was prepared in boiling ethanol for 7 h. When aqueous ammonia was used the reaction took another course and 3-aminoindazole and bis-indazol-3-ylamine **12** were formed (Scheme 1).

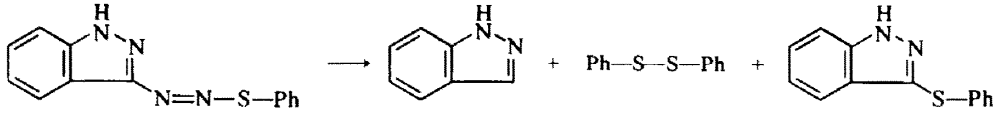
phenyl sulphide. On the other hand, photolysis yielded only indazole and diphenyl sulphide.

In order to obtain a more detailed insight into some of these reactions, experiments were performed with labelled compounds. Of primary interest was the stability of the diazo compounds, i.e. taking into account the possibility of nitrogen rearrangement. The latter process was postulated in the case of aromatic diazonium compounds and was explained earlier to proceed via an intermediate diazirine derivative **14**. An exchange of α- and β-N has been observed during the solvolysis of



Scheme 1.

diazonium ions[7,8] and a definite diazirine intermediate was later abandoned for the nitrogen scrambling reaction.[9] This rearrangement was later also disputed.[10] It should be mentioned, however, that recently a diazirine, a valence isomer of a heterocyclic diazo compound, was isolated and identified.[11] In the case of aryldiazonium salts it is now postulated that the rearrangement although occurring in a small proportion, takes place via a phenyl cation.[12,13]



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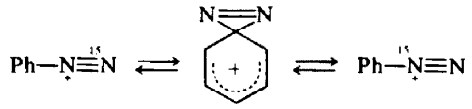

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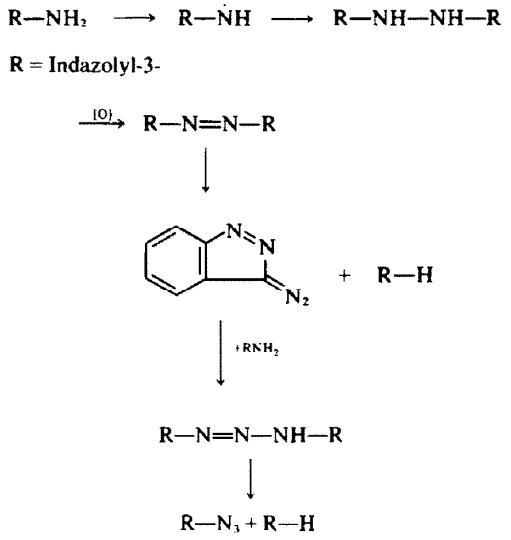
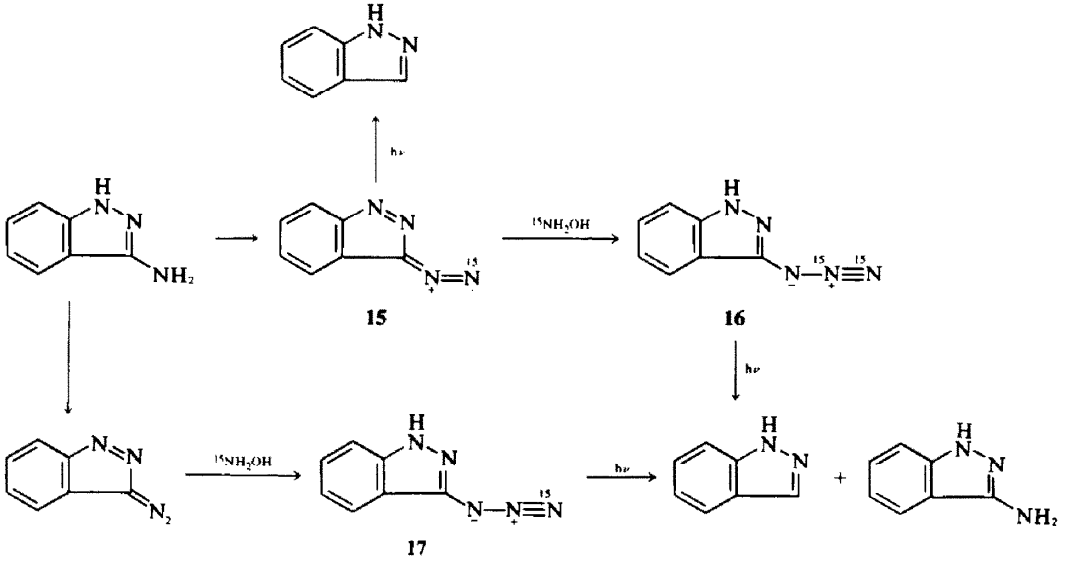
We have prepared labelled diazo(2'-^{15}N)indazole **15** which upon photolysis yielded indazole. From diazoindazole and labeled diazoindazole with labeled hydroxylamine the corresponding labeled azidoindazoles, 3'-^{15}N **17** and 2'-^{15}N, 3'-^{15}N **16** were obtained. Photochemical decomposition of these compounds revealed elimination of nitrogen without isotope rearrangement, since the 3-aminoindazole obtained showed no isotopic nitrogen in the amino group. However, before making some conclusions regarding the above processes, the peculiar behaviour of 3-aminoindazole in solution should be mentioned. In a solution of ethanol and chloroform (1:1), under the influence of light and in the presence of air this compound decomposed into a mixture of indazole and 3-azidoindazole, together with a coloured unidentified compound. In the absence of oxygen the same reaction proceeded very slowly, whereas in the dark no transformation could be observed. For these transformations a mechanism, as outlined in Scheme 2, is proposed.

An interesting observation was also made when the synthesis of 3-hydrazinoindazole was performed according to the described method of reduction of 3-diazo(3*H*)indazole.[14] When at the end of the reaction alkali was added to the reaction mixture until pH 12, 3-hydrazinoindazole, accompanied with other products was isolated. However, if the reaction mixture was made alkaline to pH 8–9, only the accompanying products were isolated. Chromatographic analysis on silica revealed indazole as the main component, accompanied with minor amounts of 3-aminoindazole and 3-azidoindazole. The



Scheme 2.



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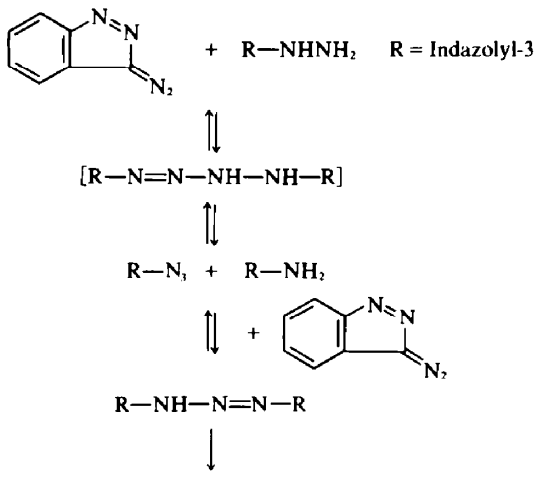

Scheme 3.

formation of these compounds is best rationalized as to proceed via a tetrazene and the amino-compound formed reacts further via a triazene as outlined in Scheme 3. The proposed mechanism is substantiated by the finding that the synthesized triazene **11f** was thermally decomposed in a methanolic solution into a mixture of indazole and 3-aminoindazole, accompanied with traces of 3-azidoindazole.

EXPERIMENTAL

M.ps were determined on a Kofler apparatus. Spectral data were obtained from a JEOL-C-60HL NMR spectrometer and Hitachi-Perkin-Elmer RMU-6L mass spectrometer. Pyrazole-3-diazonium chloride,[3] 5-carboxamido-4-diazoimidazole[6] and 3-diazo(3*H*)indazole[15] were prepared as described in the literature. With the use of $Na^{15}NO_2$ the labeled diazoindazole **15** was prepared.

General procedure for the preparation of pyrazolo(5,1-c)-as-triazines. A stirred ice cold solution of the corresponding 1,3-dicarbonyl compound (1 mmol) in ethanol (2-5 ml) was treated with 0·13 g of pyrazole-3-diazonium chloride. The reaction mixture was left to stand for 2 hr and the separated product was filtered off. Alternatively, the product was precipitated from the reaction mixture with the addition of water, or the solvent was evaporated to half its original volume and the residue was left on ice overnight. In this manner the following compounds were obtained: 3 - Acetyl - 4 - phenylpyrazolo(5,1-c) - as - triazine **1** in 55% yield, m.p. 105–106° (from ethanol). M⁺ 238; NMR ($CDCl_3$): τ = 1·61 (d, H_7), 2·68 (d, H_8), 1·90 and 2·12 (m, H_2·H_6· of Ph), 2·35 and 2·56 (m, H_3·H_4·H_5· of Ph), 6·95 (s, OMe), $J_{7,8}$ = 2·4 Hz. (Found: C, 65·53; H, 4·10; N, 23·60. Calc. for $C_{13}H_{10}N_4O$: C, 65·53; H, 4·23; N, 23·52%). 6,7,8,9 - Tetrahydropyrazolo(5,1-c) - 1,2,4 - benzotriazin - 6 - one (**2**, R = H), was obtained from 1,3-cyclohexanedione in 69% yield, m.p. 187–189° (from ethanol and DMF). M⁺ 188; NMR ($CDCl_3$): τ = 1·62 (d, H_2), 2·63 (d, H_3), 6·40 (m, 7-CH_2), 7·10 (m, 9-CH_2), 7·55 (m, 8-CH_2), $J_{2,3}$ = 2·0 Hz. (Found: C, 57·86; H, 4·29; N, 30·07. Calc. for $C_9H_8N_4O$: C, 57·44; H, 4·29; N, 29·77%). If the product was sublimed at 150°/0·1 mm and thereafter crystallized from ethanol and DMF, compound **3** was obtained, m.p. 250–255° (dec). M⁺ 186. (Found: C, 58·28; H, 3·36; N, 30·23. Calc. for $C_9H_6N_4O$: C, 58·06; H, 3·25; N, 30·10%). 8,8, - Dimethyl - 6,7,8,9 - tetrahydropyrazolo(5,1-c) - 1,2,4 - benzotriazin - 6 - one (**2**; R = Me) was prepared from 5,5-dimethyl-1,3-cyclohexanedione (dimedone) in 72% yield, m.p. 146–148° (from ethanol). M⁺ 216; NMR ($CDCl_3$): τ = 1·75 (d, H_2), 2·74 (d, H_3), 6·59 (s, 7-CH_2), 7·27 (s, 9-CH_2), 8·75 (s, 8,8-Me), $J_{2,3}$ = 2·3 Hz. (Found: C, 61·04; H, 5·74; N, 26·23. Calc. for $C_{11}H_{12}N_4O$: C, 61·09; H, 5·59; N, 25·91%).

Pyrazolo(5,1 - c)indeno(1,2 - e) - 1,2,4 - triazin - 6 - one **5**. A suspension of pyrazole-3-diazonium chloride (0·13 g) and 1,3-indanedione (0·146 g) in ethanol (3 ml) was stirred at 0° for 30 min. The product (0·2 g) which was filtered off and washed with ethanol is a mixture of **4** and **5** in a ratio of about 3 : 1. The product was crystallized from ethanol and DMF (1 : 2) and the solution was allowed to cool to 30°. Compound **5** was filtered off and after further cooling the uncyclized compound **4** was obtained. Compound **4** had m.p. 231–234° (from ethanol and DMF; at m.p. cyclization into **5** takes place). M⁺ 240; NMR (DMSO-d_6): τ = 2·26 (d, H_5), 3·62 (d, H_4), 2·17 (S, 4H of C_6H_4), −3·57 and −2·32 (s, two NH), $J_{4,5}$ = 2·2 Hz. (Found: C, 60·01; H, 3·30; N, 23·29. Calc. for $C_{12}H_8N_4O_2$: C, 60·00; H, 3·36; N, 23·33%). Compound **5** had m.p. > 270° (from ethanol and DMF, 1 : 2). M⁺ 222; NMR (DMSO-d_6, 150°): τ = 1·35 (d, H_2), 2·66 (d, H_3), 1·75 (m, H_{10}), 2·27 (m, $H_{7,8,9}$), $J_{2,3}$ = 2·8 Hz. (Found: C, 64·98; H, 2·70; N, 25·16. Calc. for $C_{12}H_6N_4O$: C, 64·80; H, 2·38; N, 25·42%).

If compound **4** was heated at its m.p. it was transformed into **5**. Alternatively, if a suspension of **5** in 5% aqueous potassium hydroxide was heated under reflux for 20 min, the red product filtered off, suspended in ethanol and acidified with conc HCl after 2 hr, the uncyclized product **4** was obtained in 60% yield.

Reaction with 2-carbethoxycyclopentanone. An ice cold solution of 2-carbethoxycyclopentanone (0·155 g) in ethanol (2 ml) was treated with pyrazole-3-diazonium chloride (0·13 g). After standing on ice for 36 hr the solvent was evaporated *in vacuo* to 1/3 of its original volume and the residue kept on ice for 5 hr. The yellow crystals were filtered off and crystallized from ethanol. Compound **6** had m.p. 147–148° (yield 26%). M⁺ 296; NMR ($CDCl_3$): τ = 2·36 (d, H_5), 3·58 (d, H_4), −1·15 (s, NH), 0·12 (s, NH), 5·65 and 5·82 (q, $COOCH_2CH_3$), 8·62 and 8·74 (t, $COOCH_2CH_3$), 7–8·45 (m, $(CH_2)_3$), $J_{4,5}$ = 2·2, J_{Et} = 7 Hz (Found: N, 19·34. Calc. for $C_{15}H_{20}N_4O_4$: N, 18·91%). If compound **6** was heated at 140–145° for 30 min and thereafter at 160°/0·1 mm for 30 min, compound **7** was obtained in about 50% yield, m.p. 210° (from ethanol). M⁺ 250 (Found: C, 52·78; H, 5·61; N, 22·64. Calc. for $C_{11}H_{14}N_4O_3$: C, 52·79; H, 5·64; N, 22·39%).

General procedure for the preparation of coupling products with 5-carboxamido-4-diazoimidazole. A suspension of the diazo compound (0·137 g) in ethanol (5 ml) was treated with the carbonyl compound (1 mmol) and the mixture stirred at room temp. for 10–20 hr. The following compounds were prepared in this manner: Compound **8a** from acetylacetone in 84% yield, m.p. 196° (purified by sublimation *in vacuo*). M⁺ 237; NMR (DMSO-d_6): τ = 2·27 (s, H_2), 2·87 (s, CH), 7·93 and 7·82 (s, Me), 2·93 (m, NH_2), −1·57 (s, NH). (Found: N, 29·21. Calc. for $C_9H_{11}N_5O_2$: N, 29·54%). Compound **8b** from ethyl acetoacetate in 89% yield, m.p. 205° (from ethanol). M⁺ 267; NMR (DMSO-d_6): τ = 2·2. (s, H_2), 2·62 (s, CH) 7·90 (s, CH_3), 5·78 (q, CH_2CH_3), 8·72 (t, CH_2CH_3) 2·96 (m, NH_2) −1·56 (s, NH), J_{Et} = 7·5 Hz. (Found: C, 45·20; H, 5·01. Calc. for $C_{10}H_{13}N_5O_4$: C, 44·94; H, 4·90%). Compound **8c** from ethyl benzoylacetate in 85% yield, m.p. 145° (from ethanol), M⁺ 329; NMR (DMSO-d_6): τ = 1·75 (s, H_2), 2·6 and 2·85 (m, Ph and NH_2), 6·0 (q, CH_2CH_3), 8·97 (t, CH_2CH_3), −2·15 (broad, NH), J_{Et} = 7·0 Hz. (Found: C, 54·35; H, 5·02. Calc. for $C_{15}H_{15}N_5O_4$: C, 54·71; H, 4·59%). Compound **8d** from diethyl acetonedicarboxylate in 87% yield, m.p. 180–182° (from ethanol). M⁺ 339; NMR (DMSO-d_6): τ = 1·17 (s, H_2), 1·3 (s, CH), 5·8 and 6·13 (q, both CH_2CH_3), 8·73 and 9·0 (t, both CH_2CH_3), 5·7 (s, CH_2COOEt), 3·0 (m, NH_2), −1·3 (broad, NH), J_{Et} = 7·5 Hz. (Found: C, 45·90; H, 5·17; N, 20·37. Calc. for $C_{13}H_{17}N_5O_6$: C, 46·01; H, 5·05; N, 20·64%). Compound **8e** from ethyl cyanoacetate in 82% yield, m.p. 230° with sublimation (from ethanol or by sublimation). M⁺ 250; NMR (DMSO-d_6): τ = 1·38 (s, H_2), 8·67 and 8·73 (t, CH_2CH_3), 5·80 (q, CH_2CH_3), 2·35 and 2·62 (broad s, NH), J_{Et} = 7·5 Hz. (Found: C, 43·50; H, 4·48. Calc. for $C_9H_9N_5O_3$: C, 43·20; H, 4·03%). Compound **8f** from 2-carbethoxycyclohexanone after 48 h at room temp. in 67% yield, m.p. 205° (from methanol). M⁺ 353; NMR (DMSO-d_6): τ = 2·45 (s, H_2), 5·75 and 6·5 (both q, two CH_2CH_3), 8·7 and 8·9 and 8·9 (both t, CH_2CH_3), 8·2–8·7 and 7·5–8·0 (m, four CH_2) J_{Et} = 7·5 Hz. (Found: N, 19·76. Calc. for $C_{15}H_{23}N_5O_4$: N, 19·82%). Compound **8g** from 2-carbethoxycyclopentanone in 76% yield, m.p. 185° (from methanol). M⁺ 311; NMR (DMSO-d_6): τ = 2·45 (s, H_2), 5·77 (q, CH_2CH_3), 8·73 (t, CH_2CH_3), 7·75 (m, 4'-CH_2), 8–8·5 (m, 2'-CH_2, 3'-CH_2), −0·65 and −2·30 (NH_2, NH, OH), J_{Et} = 7·5 Hz. (Found: C, 46·28; H, 5·47; N, 22·26. Calc. for

$C_{12}H_{17}N_4O_5$: C, 46·30; H, 5·50; N, 22·50%). Compound **8h** from benzoylacetic acid in 82% yield, m.p. 238–240° (from ethanol and DMF, 4:1). M^+ 257; NMR (DMSO-d_6): τ = 1·75 (s, H_2), 2·25 and 2·95 (m, Ph), 2·7 (m, NH_2), −4·55 (broad, NH), −2·3 (m, NH). (Found: C, 56·00; H, 4·66; N, 27·13. Calc. for $C_{12}H_{11}N_5O_2$: C, 56·02; H, 4·31; N, 27·23%). 3- Benzoyl - 8 - carboxamido - imidazo(1,5-*c*)-1,2,4-triazin-e(1*H*) one **10**. An ethanolic solution with acidified hydrochloric acid of **8c** (0·329 g) was heated under reflux for 3 hr. The reaction mixture was diluted with water and a solution of potassium hydroxide was added until alkaline reaction. The separated product was collected and crystallized from ethanol and DMF, 4:1 (yield 0·12 g, 46%), m.p. over 250°. M^+ 283; *m/e* 105 (PhCO); NMR (DMSO-d_6; 90°): τ = 1·75 (s, H_6), 2·4 (m, Ph, NH_2). (Found: C, 55·31; H, 3·46; M, 24·98. Calc. for $C_{13}H_9N_5O_3$: C, 55·12; H, 3·20; N, 24·73%).

Formation of triazenes from 3-diazo-(3H)indazole. 3-Diazo-(3*H*)indazole (0·3 g) alone or dissolved in methanol (1 ml) was added portionwise to the corresponding amine (1 ml). The separated product was filtered off or the solution was evaporated *in vacuo* at 40–50°. The products were crystallized from ethanol, yields were 67–89%. In this manner the following triazenes were prepared: 3-Ethyl-1-indazol-3'-yl triazene **11a**, m.p. 97–99°. M^+ 189. NMR (DMSO-d_6): τ = 2·10 and 2·90 (m, $H_{4,5,6,7}$) 6·50 (q, CH_2), 8·75 (t, CH_3), J_{Et} = 7·2 Hz. (Found: C, 57·46; H, 5·53; N, 37·09. Calc. for $C_9H_{11}N_5$: C, 57·12; H, 5·86, N, 37·02%). 3,3-Diethyl-1-indazol-3'-yl triazene **11b**, m.p. 139–140°. M^+ 217. (Found: C, 60·73; H, 7·12; N, 32·35. Calc. for $C_{11}H_{15}N_5$: C, 60·80; H, 6·96; N, 32·24%). 3,3-Diisopropyl-1-indazol-3'-yl triazene **11c**, m.p. 167–169°. M^+ 245. (Found: C, 63·44; H, 7·55; N, 28·32. Calc. for $C_{13}H_{19}N_5$: C, 63·64; H, 7·18; N, 28·55%). 3 - Phenyl - 1 - indazol - 3' - yl triazene **11d**, m.p. 182–183°. M^+ 237. (Found: C, 65·40; H, 4·57; N, 29·73. Calc. for $C_{13}H_{11}N_5$: C, 65·81; H, 4·67; N, 29·52%). 3 - (Pyridyl - 2') - 1 - indazol - 3'' - yl triazene **11e**. A solution of 3-diazo-(3*H*)indazole (0·144 g) and 2-aminopyridine (0·094 g) in ethanol (3 ml) was heated under reflux for 7 hr. The solvent was evaporated *in vacuo* and the residue was crystallized from ethanol (yield 0·15 g 63%), m.p. 223°. M^+ 238, *m/e* 210 (M-28, $-N_2$). (Found: C, 60·89; H, 4·67. Calc. for $C_{12}H_{10}N_6$: C, 60·49; H, 4·23%). 1,3-Di-indazol-3-yl triazene **11f**. A solution of 3-aminoindazole (0·266 g) and 3-diazo-(3*H*)indazole (0·28 g) in 2*N*-hydrochloric acid (15 ml) was left at room temp. for 20 h. Upon filtration the filtrate was neutralized with sodium bicarbonate and the product filtered off (yield 0·21 g). For analysis, the compound was crystallized from ethanol and DMF 3:1; m.p. 202–204°. M^+ 277, *m/e* 249 ($M-N_2$); NMR (DMSO-d_6): all protons exhibit a multiplet at τ = 1·4–3·1. (Found: C, 60·18; H, 4·37; Calc. for $C_{14}H_{11}N_7$: C, 60·64; H, 4·00%).

Reaction between 3-diazo(3H)indazole and ammonia. 3-diazo-(3*H*)-indazole (0·5 g) and conc. aqueous ammonia (10 ml) were shaken at room temp. for 15 min. The brown precipitate was filtered off and dissolved in methanol. Purification by TLC (Kieselgel 60 F-254, 0·25 mm; chloroform and methanol, 9:1; methanol for elution) afforded two compounds in a very small amount. One of them was identified as 3-aminoindazole (R_f value comparison with an authentic specimen; and mass spectrum M^+ 133), and the other as bis-indazol-3-yl amine **12** (M^+ 249).

3-Indazolyldiazo phenyl sulphide **13**. To an ice cold solution of 3-diazo-(3*H*)indazole (0·5 g) in ethanol (3 ml) thiophenol (0·38 g) was added and the yellow crystals were filtered off and crystallized from ethanol, m.p. 138–140° (yield 0·685 g, 78%). M^+ 254. (Found: C, 61·25; H, 3·87; N, 21·90. Calc. for $C_{13}H_{10}N_4S$: C, 61·41; H, 3·96; N, 22·04%). If the compound was heated in a solution of ethanol under reflux for 40 h, the solvent evaporated and the residue chromatographed, the following compounds could be identified: indazole (alternatively, separated from the reaction mixture by sublimation at 105°), diphenyl disulphide and 3-indazolyl phenyl sulphide. However, when a solution of **13** in methanol was irradiated at 300 mμ for 40 hr, the solvent evaporated, in the residue indazole and diphenyl disulphide could be identified.

3-Azido(3'-^{15}N)indazole **17**. To an ice sold solution of 3-diazo-(3*H*)indazole (0·144 g) in ethanol (2·5 ml) under stirring a solution of hydroxylamine hydrochloride ($^{15}NH_2OH$) (70 mg) in water (0·5 ml) was added portionwise. Thereafter the reaction mixture was evaporated *in vacuo* to 1 ml, water (4 ml) was added and the mixture was left to stand on ice for several hours. The separated crystals were filtered off (yield 68%), m.p. 95°, M^+ 160.

In similar manner the unlabeled 3-azidoindazole was prepared, m.p. 98–100° (from ethanol and water). M^+ 159; NMR ($CDCl_3$): τ = 2·70 (m, $H_{4,5,6,7}$). (Found: C, 52·59; H, 3·30; N, 43·90. Calc. for $C_7H_5N_5$: C, 52·82; H, 3·17; N, 44·01%). According to the above procedure, from 3-diazo-(3*H*)indazole (2'-^{15}*N*), the labeled 3-azido (2'-^{15}*N*, 3'-^{15}*N*)indazole **16** was prepared. M^+ 161.

Photochemical decomposition of 3-azido(3'-^{15}N)-17 or 3-azido (2'-^{15}N, 3'-^{15}N)-indazole **16**. The labeled azidoindazoles (50 mg), when separately dissolved in methanol (2 ml) and irradiated with light of wavelength 254 mμ for 5 hr, afforded a mixture of indazole and 3-aminoindazole. In both cases mass spectral examination of 3-aminoindazole revealed that there was no label in the amino group nitrogen.

Photochemical reaction of 3-diazo(2'^{15}N)indazole **15**. A solution of the diazo compound (50 mg) in methanol (2 ml) was irradiated for 7 days with light of 254 mμ. The solution was then evaporated and the residue was identified as indazole (yield 83%).

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