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Studies on 2,5-Diaryl-2,4-dihydro-3*H*-pyrazol-3-ones. I. Synthesis of Highly Substituted 1*H*-Indazoles Using Tautomeric 2,5-Diaryl-2,4-dihydro-3*H*-pyrazol-3-ones[1)]

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The reaction of 2-aryl-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (**1**) with acetone gave 2-aryl-4-(1-methylethylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (**2**) in nearly quantitative yields, and these products reacted further with acetone in the presence of triethylamine (NEt_3) as a catalyst to give 1-aryl-4,6,6-trimethyl-3-phenyl-1,6-dihydropyrano[2,3-*c*]pyrazoles (**3**).

Reaction of **3** with dimethyl acetylenedicarboxylate (DMAD) or diethyl acetylenedicarboxylate (DEAD) in dimethylformamide (DMF) at reflux gave 1-aryl-4-methyl-3-phenyl-1*H*-indazole-6,7-dicarboxylate (**7**) in high yields. Thus, a new and convenient route for the synthesis of highly substituted 1*H*-indazoles has been developed.

Keywords——tautomerism; 2,4-dihydro-3*H*-pyrazol-3-one; 1,6-dihydropyrano[2,3-*c*]-pyrazole; 1*H*-indazole; dimethyl acetylenedicarboxylate; diethyl acetylenedicarboxylate; condensation; Diels–Alder reaction

The chemistry of pyrazoles has been extensively investigated because of the potential of these compounds as pharmaceuticals and their applications in the dye and photographic industries. In the course of studies aimed at finding pyrazole-based anti-inflammatory compounds, we have developed a general procedure to prepare 1,3-diaryl-4,6,6-trimethyl-1,6-dihydropyrano[2,3-*c*]pyrazoles from the corresponding 2,5-diaryl-2,4-dihydro-3*H*-pyrazol-3-ones.[1a)] As 1,3-diaryl-4,6,6-trimethyl-1,6-dihydropyrano[2,3-*c*]pyrazoles have a diene moiety in the molecule, their reaction with strong dienophiles was also examined. Through this reaction, highly substituted 1*H*-indazoles were obtained in nearly quantitative yields.[1b)] In this paper we present the experimental details of the above conversion.

Synthesis of 1,3-Diaryl-4,6,6-trimethyl-1,6-dihydropyrano[2,3-*c*]pyrazoles Using Tautomeric 2,5-Diaryl-2,4-dihydro-3*H*-pyrazol-3-ones

It is known that active methylenes at the 4-position of 2,4-dihydro-3*H*-pyrazol-3-ones such as **1** react with ketones or aldehydes to give the corresponding 4-alkylidene-2,4-dihydro-3*H*-pyrazol-3-ones such as **2** in nearly quantitative yields.[2)]

Since they have an enone moiety in the molecule, 4-alkylidene-2,4-dihydro-3*H*-pyrazol-3-ones such as **2** react with enol ethers to give 1,4,5,6-tetrahydropyrano[2,3-*c*]pyrazoles in a Diels–Alder fashion.[3)] In the course of our investigation aimed at using these 4-alkylidene-2,4-dihydro-3*H*-pyrazol-3-ones as reactive intermediates, we found a general conversion of **2** into 1,6-dihydropyrano[2,3-*c*]pyrazoles (**3**) in high yields.

Treatment of 2-aryl-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (**1**) with acetone under reflux for 24 h afforded 2-aryl-4-(1-methylethylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (**2**) in nearly quantitative yields. The structures of **2** were assigned on the basis of elemental analysis and spectroscopic data. For example, in the case of **2a** the molecular formula was confirmed to be $C_{18}H_{16}N_2O$ by elemental analysis and mass spectroscopy (M^+: 276). The proton magnetic resonance (^{1}H-NMR) spectrum revealed two singlets at 1.93 ppm (3H) and 2.62 ppm (3H) due to two methyls of the 1-methylethylidene group at the 4-position and an aromatic multiplet at 7.60—8.10 ppm (10H).

The signals corresponding to the methylene protons of **1** had disappeared (in $CDCl_3$ **1** presents its CH form). The carbon nuclear magnetic resonance (^{13}C-NMR) spectrum revealed two quartets at 26.05 and 22.96 ppm due to the two methyl carbons of the 1-methylethylidene group at the 4-position. The signal due to the methylene carbon at the 4-position of **1** had disappeared. The infrared (IR) spectrum showed a strong carbonyl absorption in the 1690 cm^{-1} region (the physical properties of **2** are summarized in Tables IV and VII in the experimental section).

Treatment of **2** with acetone in the presence of triethylamine under reflux for 12 h afforded 1-aryl-4,6,6-trimethyl-3-phenyl-1,6-dihydropyrano[2,3-*c*]pyrazoles (**3**) in high yields.

TABLE I. 2-Aryl-4-(1-methylethylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (**2**)

Compd. No.	R_1	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	Br	Cl	N
2a	H	116—117	90	$C_{18}H_{16}N_2O$	78.23	5.84			10.14
					(78.48	5.70			10.30)
2b	Br	155—157	90	$C_{18}H_{15}BrN_2O$	60.86	4.26	22.49	—	7.89
					(61.02	4.16	22.36		7.89)
2c	Cl	129—130	90	$C_{18}H_{15}ClN_2O$	69.57	4.86	—	11.41	9.01
					(69.40	4.95		11.32	9.04)
2d	Me	114—115	88	$C_{19}H_{18}N_2O$	78.59	6.25	—	—	9.65
					(78.64	6.34			9.63)

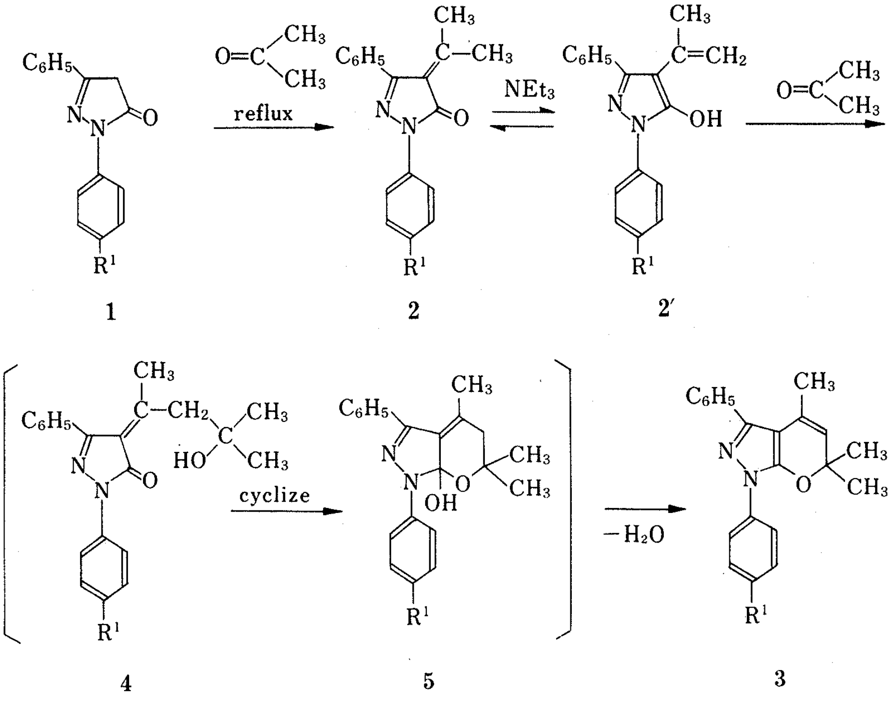

Chart 1

TABLE II. 1-Aryl-4,6,6-trimethyl-3-phenyl-1,6-dihydropyrano-[2,3-*c*]pyrazoles (**3**)

Compd. No.	R_1	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd (Found) C	H	Br	Cl	N
3a	H	110—111	70	$C_{21}H_{20}N_2O$	79.71 (79.93	6.37 6.20	—	—	8.85 8.64)
3b	Br	126—127	60	$C_{21}H_{19}BrN_2O$	63.81 (64.02	4.84 4.76	20.21 20.03	—	7.09 7.03)
3c	Cl	102—104	80	$C_{21}H_{19}ClN_2O$	71.89 (72.04	5.46 5.55	—	10.10 9.82	7.98 7.97)
3d	Me	95—97	65	$C_{22}H_{22}N_2O$	79.97 (80.07	6.71 6.80	—	—	8.48 8.44)

A plausible reaction mechanism for the formation of **3** is illustrated in Chart 1. 2-Aryl-4-(1-methylethylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones are isomerized to their tautomeric OH forms (**2′**) by the action of NEt_3, and the latter react with one mol of acetone to give adducts **4**. The adducts **4** cyclize to give 1,5,6,7a-tetrahydropyrano[2,3-*c*]pyrazoles such as **5**, which dehydrate (catalyzed by NEt_3) to afford **3** as final products. This reaction proceeds in a basic medium; in the absence of NEt_3, no conversion of **2** to **3** occurred even under reflux for 100 h. This observation suggests that the formation of tautomeric OH forms (**2′**) catalyzed by NEt_3 is a key step of the above conversion.

The structures of **3** were assigned on the basis of elemental analysis and spectroscopic data. For example, in the case of **3a**, the molecular formula was confirmed to be $C_{21}H_{20}N_2O$ by elemental analysis and mass spectroscopy (M^+: *m/e* 316). The ^{1}H-NMR spectrum revealed a singlet at 1.57 ppm (6H) due to two methyls (6,6-dimethyl substituents), a doublet at 1.78 ppm (3H) due to the 4-methyl substituent, a quartet at 4.93 ppm (1H) due to the olefinic proton at the 5-position of the ring and an aromatic multiplet at 7.30—8.10 ppm (10H). The ^{13}C-NMR spectrum revealed two types of methyl carbons at 27.85 and 19.17 ppm due to the 6- and 4-methyl substituents, and a carbon at 84.48 ppm (6-position on the ring). The signal due to the carbonyl carbon at the 3-position of **2** had disappeared.

The IR spectrum showed an olefinic $C=C$ absorption band in the 1640 cm^{-1} region and no strong $C=O$ absorption band was observed (the physical properties of **3** are summarized in Tables V and VIII in the experimental section).

Synthesis of Highly Substituted 1*H*-Indazoles

There are three classical methods for the synthesis of the 1*H*-indazole skeleton. The most frequently used route for the synthesis of 1*H*-indazoles is the diazotization of anilines having a carbon substituent *ortho* to the amino group[4)] (type A). Dehydration of phenyl ketone oximes having an amino group *ortho* to the oximes also gives 1*H*-indazoles under acid catalysis[5)] (type B). Further, 2-halogeno-5-nitrobenzaldehyde benzoylhydrazones cyclize to 1*H*-indazoles at high temperature in a basic medium[6)] (type C). These methods have several limitations, as might be anticipated from the reaction conditions required. In the type A procedure, one must isolate 1*H*-indazoles from by-products such as phenols and azo compounds.

In the type B procedure, isomerization to 2*H*-indazoles always occurs. In the case of type C, severe reaction conditions may be necessary. In addition, in order to facilate the removal of hydrogen halide, nitro substituents at the 3- and/or 5-position are necessary in some cases.

Thus, systematic synthetic approaches to highly substituted 1*H*-indazoles have not been reported so far. We report herein a systematic one-pot synthesis of highly substituted 1*H*-indazoles using **3** as reactive intermediates under mild reaction conditions. Since they have a diene moiety in the molecule, compound **3** may be anticipated to react with strong dienophiles such as dimethyl acetylenedicarboxylate (DMAD, **6a**) or diethyl acetylenedicarboxylate (DEAD, **6b**). Treatment of **3a** with DMAD in dimethylformamide (DMF) at reflux for 6 h afforded dimethyl 4-methyl-1,3-diphenyl-1*H*-indazole-6,7-dicarboxylate (**7a**) in 82% yield. The structure of **7a** was assigned on the basis of elemental analysis and spectroscopic data.

The molecular formula was confirmed to be $C_{24}H_{20}N_2O_4$ by elemental analysis and mass spectroscopy (M^+: *m/e* 400). The ^{1}H-NMR spectrum revealed a broad singlet at 2.38 ppm (3H) due to the methyl group at the 4-position of the ring, two singlets at 3.29 ppm (3H) and 3.80 ppm (3H) due to two carbomethoxy substituents at the 6- and 7-positions on the ring and an aromatic multiplet at 7.40—7.63 ppm (11H). The ^{13}C-NMR spectrum showed two signals at 166.76 and 166.47 ppm due to the carbomethoxy carbonyl carbons at the 6- and 7-positions of the ring. The signals due to methyl carbons at the 6-position of **3a** and the 6-position carbon of **3a** had disappeared. The IR spectrum showed two carboxyl absorption bands at 1740 and 1710 cm^{-1}. The absorption band at 1640 cm^{-1} due to the olefinic C=C had disappeared (the physical properties of 7 are summarized on Tables VI and IX in the

TABLE III. Dialkyl 1-Aryl-4-methyl-3-phenyl-1*H*-indazole-6,7-dicarboxylate (**7**)

Compd. No.	R_1	R_2	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd (Found)				
						C	H	Br	Cl	N
7a	H	Me	180—182	82	$C_{24}H_{20}N_2O_4$	71.98	5.03	—	—	7.00
						(71.72	4.98			6.95)
7b	Br	Me	182—183	80	$C_{24}H_{19}BrN_2O_4$	60.14	4.00	16.67	—	5.04
						(60.08	4.08	16.43		4.89)
7c	Cl	Me	151—152	75	$C_{24}H_{19}ClN_2O_4$	66.29	4.40	—	8.15	6.40
						(66.39	4.42		8.03	6.50)
7d	Me	Me	141—142	82	$C_{25}H_{22}N_2O_4$	72.45	5.35	—	—	6.76
						(72.26	5.50			6.60)
7e	H	Et	160—162	72	$C_{26}H_{24}N_2O_4$	72.88	5.65	—	—	6.54
						(73.03	5.64			6.76)
7f	Br	Et	191—193	72	$C_{26}H_{23}BrN_2O_4$	61.55	4.57	15.75	—	5.52
						(61.38	4.43	15.95		5.62)
7g	Cl	Et	143—144	70	$C_{26}H_{23}ClN_2O_4$	67.46	5.01	—	7.66	6.05
						(67.67	5.16		7.56	5.98)
7h	Me	Et	130—131	80	$C_{27}H_{26}N_2O_4$	73.28	5.92	—	—	6.33
						(73.03	5.94			6.32)

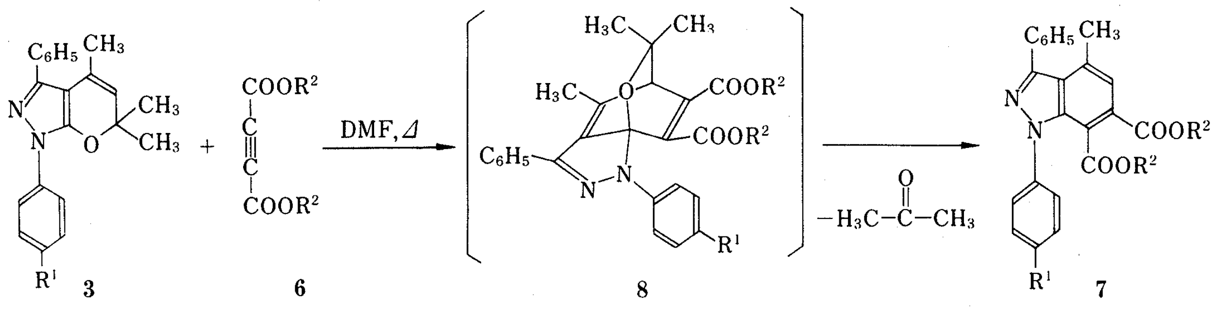

Chart 2

experimental section). Similarly the 1*H*-indazoles **7b**—**h** were obtained in high yields and the results are listed in Table III.

A plausible reaction mechanism for the formation of **7** is illustrated in Chart 2; **3** reacts with **6** to give the Diels–Alder adduct **8**. The adduct **8** spontaneously expels acetone to afford **7** in high yield. A similar type of reaction (Diels–Alder addition-elimination procedure) has been widely reported.[7)]

Conclusion

The most interesting feature of the present conversion is the application of tautomeric

TABLE IV. Physical Properties of 2-Aryl-4-(1-methylethylidene)-5-phenyl-3*H*-pyrazol-3-ones (**2**)

Compd. No.	R_1	^{1}H-NMR ($CDCl_3$) δ:	IR ν_{KBr} cm^{-1}	UV $\varepsilon_{\max}^{\text{ethanol}}$ nm (log ε)	MS *m*/*e* (Rel. intensity)
2a	H	1.93 (s, 3H); 2.62 (s, 3H); 7.60—8.10 (m, 10H)	1690, 1600	259 (4.20)	276 (M^+, 100%) 261 (95)
2b	Br	1.93 (s, 3H); 2.60 (s, 3H); 7.33 (d, 2H, $J=8$ Hz); 7.30—7.40 (m, 5H); 7.92 (d, 2H, $J=8$ Hz)	1690, 1620	267 (4.23)	356, 354 (M^+, 100, 100%); 341, 339 (90, 90)
2c	Cl	1.90 (s, 3H); 2.60 (s, 3H); 7.20 (d, 2H, $J=10$ Hz); 7.20—7.40 (m, 5H); 7.90 (d, 2H, $J=10$ Hz)	1685, 1625	265 (4.28)	312, 310 (M^+, 70, 100%); 295 (90)
2d	Me	1.90 (s, 3H); 2.33 (s, 3H); 2.60 (s, 3H); 7.13 (d, 2H, $J=8$ Hz); 7.30—7.40 (m, 5H); 7.77 (d, 2H, $J=8$ Hz)	1685, 1625	260 (4.40)	290 (M^+, 100%) 275 (95)

TABLE V. Physical Properties of 1-Aryl-4,6,6-trimethyl-3-phenyl-1,6-dihydropyrano[2,3-*c*]pyrazoles (**3**)

Compd. No.	R_1	^{1}H-NMR ($CDCl_3$) δ:	IR ν_{KBr} cm^{-1}	UV $\varepsilon_{\max}^{\text{ethanol}}$ nm (log^K ε)	MS *m*/*e* (Rel. intensity)
3a	H	1.57 (s, 6H); 1.78 (d, 3H, $J=1.5$ Hz); 4.93 (q, 1H, $J=1.5$ Hz); 7.30—8.00 (m, 10H)	2950, 1640, 1595	261 (4.11)	316 (M^+, 30%); 301 (100)
3b	Br	1.55 (s, 6H); 1.75 (d, 3H, $J=1.5$ Hz); 4.91 (q, 1H, $J=1.5$ Hz); 7.20—7.80 (m, 9H)	2990, 1630, 1595	267 (4.25)	396, 394 (M^+, 33, 55%); 381, 379 (98, 100)
3c	Cl	1.57 (s, 6H); 1.75 (d, 3H, $J=1.5$ Hz); 4.91 (q, 1H, $J=1.5$ Hz); 7.20—7.80 (m, 9H)	2975, 1625, 1600	268 (4.24)	352, 350 (M^+, 15, 30%); 337, 335 (37, 100)
3d	Me	1.55 (s, 6H); 1.76 (d, 3H, $J=1.6$ Hz); 2.36 (s, 3H); 4.90 (q, 1H, $J=1.6$ Hz); 7.20—7.80 (m, 9H)	2975, 1630, 1615, 1605	265 (4.29)	330 (M^+, 50%); 315 (100)

2,4-dihydro-3*H*-pyrazol-3-ones in organic synthesis. Although a rigorous study of the tautomerism of 2,4-dihydro-3*H*-pyrazol-3-ones has been reported,$^{8)}$ no application of these characteristics in organic synthesis has been described. In our method, the key step for the formation of **3** (or final product **7**) is the tautomeric conversion of **2** to **2′** catalyzed by NEt_3. Using **3** as a reactive diene, one may easily obtain highly substituted 1*H*-indazoles in yields of *ca.* 50% starting from 2,5-diaryl-2,4-dihydro-3*H*-pyrazol-3-ones (**1**).

Further studies are in progress to extend the scope of this method.

Experimental

All melting points were recorded on a Yanagimoto melting point apparatus, and are uncorrected. IR spectra were measured with a Jasco A-3 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra (^{1}H-NMR 199.50 MHz and ^{13}C-NMR 50.10 MHz) were recorded with a JEOL JNM-FX-200 spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Ultraviolet (UV) spectra were recorded with a Shimadzu UV-300 spectrometer.

Column chromatography was carried out with Kieselgel 60 (70—230 mesh) using benzene as the eluent. Mass spectra were measured with a Hitachi-MU-7MG mass spectrometer.

General Procedure for the Preparation of 2-Aryl-4-(1-methylethylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones (2)——A solution of 2-aryl-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**1**, 10 mmol) in dry acetone (300 ml) was refluxed, and the reaction was continued till **1** was no longer detectable by thin-layer chromatography (TLC, *ca.* 24 h). The reaction mixture was evaporated *in vacuo* at room temperature to give a dark brown solid, which was recrystallized from ethyl alcohol to give **2** as yellow prisms.

General Procedure for the Preparation of 1-Aryl-4,6,6-trimethyl-5-phenyl-1,6-dihydropyrano[2,3-*c*]pyrazoles (3)

Table VI. Physical Properties of Dialkyl 1-Aryl-4-methyl-3-phenyl-1*H*-indazole-6,7-dicarboxylate (7)

Compd. No.	R_1	R_2	^{1}H-NMR ($CDCl_3$) δ:	IR ν_{KBr} cm^{-1}	UV $\varepsilon_{max}^{ethanol}$ nm (log ε)	MS *m/e* (Rel. intensity)
7a	H	Me	2.38 (s, 3H); 3.29 (s, 3H); 3.80 (s, 3H); 7.40—7.63 (m, 11H)	1740, 1710 1595, 1268	246 (4.62) 333 (3.96)	400 (M^+, 100%); 337 (45)
7b	Br	Me	2.39 (s, 3H); 3.40 (s, 3H); 3.90 (s, 3H); 7.35—7.71 (m, 10H)	1730, 1725 1595, 1280	234 (4.89) 335 (3.94)	480, 478 (M^+, 95, 100%)
7c	Cl	Me	2.39 (s, 3H); 3.40 (s, 3H); 3.90 (s, 3H); 7.45—7.62 (m, 10H)	1730, 1725 1595, 1290	250 (4.56) 332 (4.08)	436, 434 (M^+, 25, 100%)
7d	Me	Me	2.39 (s, 3H); 2.43 (s, 3H); 3.32 (s, 3H); 3.90 (s, 3H); 7.26—7.60 (m, 10H)	1735, 1730 1600, 1280	253 (4.70) 339 (4.09)	414 (M^+, 100%) 351 (25)
7e	H	Et	1.07 (t, 3H, $J=7$ Hz); 1.35 (t, 3H, $J=7$ Hz); 2.39 (s, 3H); 3.65 (q, 2H, $J=7$ Hz); 4.35 (q, 2H, $J=7$ Hz); 7.35—7.63 (m, 11H)	1735, 1715 1595, 1280	244 (4.69) 335 (4.05)	428 (M^+, 70%) 301 (100)
7f	Br	Et	1.11 (t, 3H, $J=8$ Hz); 1.37 (t, 3H, $J=8$ Hz); 2.39 (s, 3H); 3.75 (q, 2H, $J=8$ Hz); 4.38 (q, 2H, $J=8$ Hz); 7.35—7.71 (m, 10H)	1725, 1720 1585, 1260	240 (4.52) 338 (4.11)	508, 506 (M^+, 100, 98%)
7g	Cl	Et	1.12 (t, 3H, $J=8$ Hz); 1.37 (t, 3H, $J=8$ Hz); 2.39 (s, 3H); 3.75 (q, 2H, $J=8$ Hz); 4.37 (q, 2H, $J=8$ Hz); 7.42—7.62 (m, 10H)	1725, 1715, 1590, 1270	249 (4.78) 336 (4.34)	464, 462 (M^+, 25, 100%); 335 (25)
7h	Me	Et	1.09 (t, 3H, $J=8$ Hz); 1.38 (t, 3H, $J=8$ Hz); 2.39 (s, 3H); 2.43 (s, 3H); 3.67 (q, 2H, $J=8$ Hz); 4.35 (q, 2H, $J=8$ Hz); 7.26—7.60 (m, 10H)	1735, 1720, 1590, 1280	254 (4.83) 330 (4.15)	442 (M^+, 100%) 351 (15)

Table VII. ^{13}C-NMR Data of 2-Aryl-4-(1-methylethylidene)-5-phenyl-3*H*-pyrazol-3-ones (**2**) in $CDCl_3$

Compd.	δ Values from tetramethylsilane
2a	166.77 (s), 163.44 (s), 150.96 (s), 138.51 (s), 134.32 (s), 129.17 (d), 128.80 (d, 2C), 128.66 (d, 2C), 128.51 (d), 124.79 (d, 2C), 124.62 (s), 119.12 (d, 2C), 26.05 (q), 22.96 (q)
2b	168.28 (s), 163.42 (s), 151.30 (s), 137.66 (s), 134.18 (s), 131.67 (d, 2C), 129.36 (d), 128.80 (d, 2C), 128.61 (d, 2C), 124.54 (s), 120.46 (d, 2C), 117.61 (s), 26.13 (q), 23.08 (q)
2c	168.28 (s), 163.42 (s), 151.28 (s), 137.22 (s), 134.20 (s), 129.80 (s), 129.34 (d), 128.80 (d, 2C), 128.68 (d, 2C), 128.61 (d, 2C), 124.52 (s), 120.12 (d, 2C), 26.10 (q), 23.06 (q)
2d	167.19 (s), 163.42 (s), 150.74 (s), 136.17 (s), 134.57 (s), 130.55 (s), 129.17 (d), 128.90 (d, 2C), 128.56 (d, 2C), 125.98 (d, 2C), 124.86 (s), 119.19 (d, 2C), 26.03 (q), 22.96 (q), 20.92 (q)

Table VIII. ^{13}C-NMR Data of 1-Aryl-4,6,6-trimethyl-1,6-dihydropyrano[2,3-*c*]pyrazoles (**3**) in $CDCl_3$

Compd.	δ Values from tetramethylsilane
3a	151.08 (s), 148.29 (s), 138.60 (s), 134.49 (s), 131.55 (s), 129.31 (d, 2C), 128.87 (d, 2C), 128.07 (d), 127.97 (d, 2C), 125.88 (d), 120.70 (d, 2C), 118.78 (d), 84.48 (s), 27.85 (q, 2C), 19.17 (q)
3b	151.18 (s), 148.70 (s), 137.73 (s), 134.27 (s), 131.96 (d, 2C), 131.40 (s), 129.31 (d, 2C), 128.24 (d), 128.02 (d, 2C), 127.61 (s), 121.99 (d, 2C), 119.07 (s), 118.93 (d), 84.89 (s), 27.88 (q, 2C), 19.12 (q)
3c	151.16 (s), 148.65 (s), 137.22 (s), 134.27 (s), 131.33 (s), 129.31 (d, 2C), 129.02 (d, 2C), 128.26 (d), 127.80 (s), 128.02 (d, 2C), 121.72 (d, 2C), 120.04 (s), 118.95 (d), 84.87 (s), 27.88 (q, 2C), 19.12 (q)
3d	151.01 (s), 148.09 (s), 136.24 (s), 135.73 (s), 134.64 (s), 131.68 (s), 129.43 (d, 4C), 128.78 (s), 128.07 (d), 127.97 (d, 2C), 120.92 (d, 2C), 118.80 (d), 84.41 (s), 27.88 (q, 2C), 20.94 (q), 19.17 (q)

——A solution of **2** (10 mmol) and dry triethylamine (10.10 g, 100 mmol) in acetone (150 ml) was refluxed, and the reaction was continued till **2** was no longer detectable by TLC (*ca.* 12 h). The reaction mixture was evaporated *in vacuo* at room temperature to give a dark brown oily residue, which was chromatographed on silica gel (eluent, benzene). The product **3** was obtained from the first fraction as a white precipitate, which was recrystallized from ethyl alcohol or iso-propyl alcohol to give **3** as colorless needles in *ca.* 70% yield.

General Procedure for the Formation of Dialkyl 1-Aryl-4-methyl-3-phenyl-1*H*-indazole 6,7-dicarboxylate (7)—— A solution of **3** (10 mmol) and dialkyl acetylenedicarboxylate (**6**, 15 mmol) in dry dimethylformamide (100 ml) was refluxed for 6 h. The mixture was then evaporated *in vacuo* at 50—60 °C to give a dark brown oily residue, which was crystalized from iso-propyl alcohol to give a white precipitate.

The white precipitate was further recrystallized from iso-propyl alcohol–acetone (10 : 1) to give **7** as colorless prisms in *ca.* 80% yield.

Table IX. ^{13}C-NMR Data of Dialkyl 1-Aryl-4-methyl-3-phenyl-1*H*-indazole-6,7-dicarboxylate (**7**) in $CDCl_3$

Compd.	δ Values from tetramethylsilane
7a	166.76 (s), 166.47 (s), 147.58 (s), 139.81 (s), 137.21 (s), 134.32 (s), 133.56 (s), 130.32 (d, 2C), 128.92 (d, 2C), 128.83 (d), 128.62 (d), 128.07 (d, 2C), 127.57 (s), 127.22 (d, 2C), 125.41 (s), 122.93 (d), 117.41 (s), 52.53 (q), 51.98 (q), 20.24 (q)
7b	166.65 (s), 166.48 (s), 148.04 (s), 138.80 (s), 137.17 (s), 134.54 (s), 133.33 (s), 132.08 (d, 2C), 130.26 (d, 2C), 128.78 (d), 128.70 (d, 2C), 128.17 (d, 2C), 127.80 (s), 125.57 (s), 123.21 (d), 122.72 (s), 117.17 (s), 52.62 (q), 52.12 (q), 20.21 (q)
7c	166.70 (s), 166.53 (s), 148.07 (s), 138.36 (s), 138.21 (s), 137.49 (s), 134.91 (s), 132.81 (s), 130.33 (d, 2C), 129.09 (d, 2C), 128.56 (d, 2C), 128.44 (d), 127.66 (d, 2C), 127.54 (s), 124.42 (s), 122.79 (d), 117.13 (s), 52.64 (q), 52.18 (q), 19.48 (q)
7d	166.80 (s), 166.58 (s), 147.39 (s), 138.92 (s), 137.29 (s), 134.25 (s), 133.71 (s), 130.55 (s), 130.41 (d, 2C), 129.46 (d, 2C), 128.58 (d), 128.10 (d, 2C), 127.34 (s), 127.17 (d, 2C), 125.40 (s), 122.84 (d), 117.40 (s), 52.54 (q), 52.00 (q), 21.21 (q), 20.26 (q)
7e	166.44 (s), 166.15 (s), 147.60 (s), 140.01 (s), 137.12 (s), 134.20 (s), 133.62 (s), 130.32 (d, 2C), 128.89 (d, 2C), 128.74 (d), 128.60 (d), 128.07 (d, 2C), 127.08 (d, 2C), 127.08 (d, 2C), 127.57 (s), 125.38 (s), 123.00 (d), 117.50 (s), 61.61 (t), 61.47 (t), 20.24 (q), 14.13 (q), 13.61 (q)
7f	166.48 (s), 166.18 (s), 146.92 (s), 140.31 (s), 137.14 (s), 134.42 (s), 133.01 (s), 132.94 (d, 2C), 130.01 (d, 2C), 128.66 (d, 2C), 128.17 (d), 127.83 (s), 127.54 (d, 2C), 125.28 (s), 123.28 (d), 122.65 (s), 117.61 (s), 62.23 (t), 61.74 (t), 20.21 (q), 14.06 (q), 13.14 (q)
7g	166.36 (s), 166.14 (s), 148.09 (s), 138.15 (s), 138.12 (s), 137.41 (s), 134.69 (s), 132.86 (s), 130.26 (d, 2C), 129.02 (d, 2C), 128.73 (d), 128.41 (d, 2C), 127.63 (d, 2C), 125.49 (s), 124.35 (s), 122.70 (d), 117.25 (s), 61.69 (t, 2C), 19.46 (q), 14.13 (q), 13.60 (q)
7h	166.41 (s), 166.21 (s), 147.36 (s), 138.80 (s), 137.46 (s), 134.06 (s), 130.36 (d, 2C), 129.38 (d, 2C), 128.53 (d), 128.05 (d, 2C), 127.93 (s), 127.00 (d, 2C), 125.27 (s), 122.89 (d), 117.61 (s), 61.59 (t), 61.45 (t), 21.19 (q), 20.24 (q), 14.13 (q), 13.57 (q)

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