Reactions of 2-Diazo-1,2-Diphenylethanone and Diphenyldiazomethane with Ketohydrazones

Girija Shankar Singh, Surendra Bahadur Singh, and Kailash Nath Mehrotra*

Department of Chemistry, Banaras Hindu University, Varanasi-221 005, India

(Received August 30, 1983)

The reactions of 2-diazo-1,2-diphenylethanone (**1**) with ketohydrazones (**3a**—**c**) in equimolecular ratio yield (diphenylacetyl)hydrazones (**4a**—**c**) of the corresponding benzophenones which on further treatment with **1** in equimolecular ratio leads to 1-diphenylacetylazo-1,1,3,3-tetraaryl-2-propanones (**5a**—**c**). The product **5a** is also obtained in the reaction of **1** with benzophenone hydrazone (**3a**) in 2 : 1 molecular ratio. The bis(acetylacetonato)copper(II)-catalyzed reaction of **1** and also of diphenyldiazomethane (**2**) with ketohydrazones (**3**) affords ketazines (**6**). The mechanistic route for the formation of products is discussed.

The thermal decomposition of 2-diazo-1,2-diphenylethanone (**1**) in the presence of amines has been observed to yield diphenylacetamides.[1] Using bis(acetylacetonato)copper(II) as a catalyst in the above reaction the products formed are benzilmonoimines.[1] Copper powder,[2] salts,[3] and complexes[4] have been employed earlier as these are known to prevent Wolff rearrangement of carbenes to ketenes in the decomposition of α-diazo ketones. Bis(acetylacetonato)copper(II)-catalyzed decomposition of diphenyldiazomethane (**2**) in the presence of primary amines gives benzophenone (*N*-substituted imines).[5] The reaction of **1** with *N*-substituted imines has been reported to yield 2-azetidinones[6] which are also formed in the reaction of diphenylketene with fluorenone acetyl (or benzoyl) hydrazones.[7] The thermal decomposition of **1** in the presence of monoanils of benzil has been observed to yield spiro-2-azetidinones.[8] The reaction of **1** with 1,1-diphenylmethanimine has been reported to form a 2-azetidinone derivative.[9] We now report the thermal decomposition of 2-diazo-1,2-diphenylethanone (**1**) in the presence of ketohydrazones (**3a**—**c**) to give (diphenylacetyl) hydrazones (**4a**—**c**) of the corresponding benzophenones, these on further reaction with **1** yield 1-diphenylacetylazo-1,1,3,3-tetraaryl-2-propanones (**5a**—**c**). In each step the reacting species is diphenylketene. The reaction between **1** and **3a** in 2 : 1 molecular ratio also gives the product **5a**. The bis(acetylacetonato)copper(II)-catalyzed decomposition of **1** and also of diphenyldiazomethane (**2**) in the presence of ketohydrazones **3** form ketazines **6a**—**g** in which benzoylphenylcarbene and diphenylcarbene, respectively, are the reacting species.

Results and Discussion

An equimolecular mixture of 2-diazo-1,2-diphenylethanone (**1**) and benzophenone hydrazone (**3a**) was heated to reflux in dry benzene for 8 h under a stream of nitrogen. The reaction product was separated by fractional crystallization from ethanol; it consisted of benzophenone(diphenylacetyl)hydrazone (**4a**). The structural assignment of **4a** was made on the basis of its analytical and spectral data.

Similar treatment of hydrazones **3b** and **3c** gave (diphenylacetyl)hydrazones **4b** and **4c**, respectively, (identified on the basis of their analytical and spectral data).

Treatment of compounds **4a**—**c** with **1** in equimolecular ratio gave 1-diphenylacetylazo-1,1,3,3-tetraaryl-2-propanones (**5a**—**c**) characterized on the basis of their analytical and spectral data. The product 1-diphenylacetylazo-1,1,3,3-tetraphenyl-2-propanone(**5a**) was also obtained in the reaction of **1** with **3a** in 2 : 1 molecular ratio. In the above reaction, benzophenone (diphenylacetyl)hydrazone (**4a**) seems to be an intermediate as shown in Scheme 1.

The product mixture, obtained from the bis(acetylacetonato)copper(II)-catalyzed reaction of **1** with **3a** in dry benzene, was separated by elution chromatography and crystallized from ethanol; it gave 2-diphenylmethylenehydrazono-1,2-diphenylethanone (**6a**). The structure of **6a** was assigned on the basis of analytical and spectral data.

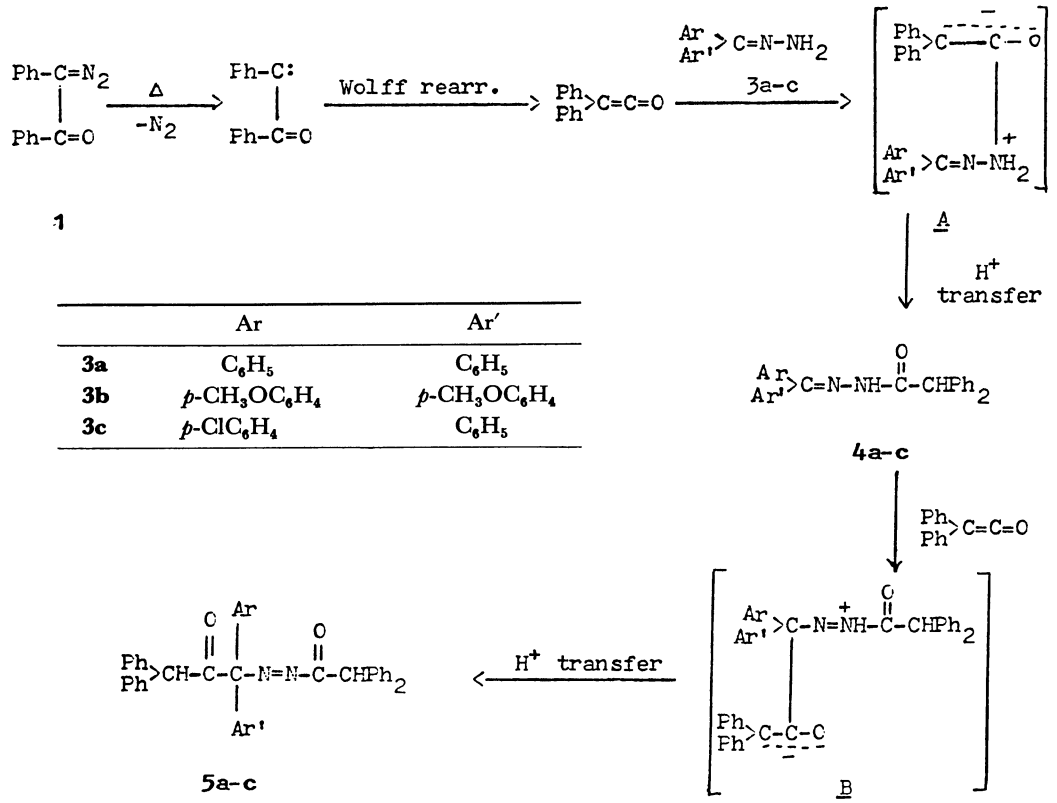
Similar treatment of **1** with hydrazones **3b**—**f** gave 2-diarylmethylenehydrazono-1,2-diphenylethanones(**6b**—**f**) identified on the basis of their analytical and spectral data. Authentic samples of the products **6a**—**f** were prepared following the reported method[10] for comparison (analytical and spectral data).

When diphenyldiazomethane (**2**) was allowed to react with benzophenone hydrazone (**3a**), in an analogous manner, a yellow solid was obtained which was identified as benzophenone azine (**6g**) on the basis of its analytical and spectral data and also comparison (IR, NMR, and mp) with an authentic sample, prepared according to the method reported.[11]

Similar treatment of **2** with benzil monohydrazone (**3d**) afforded yellow crystalline product, characterized as ketazine **6a** on the basis of its analytical and spectral data.

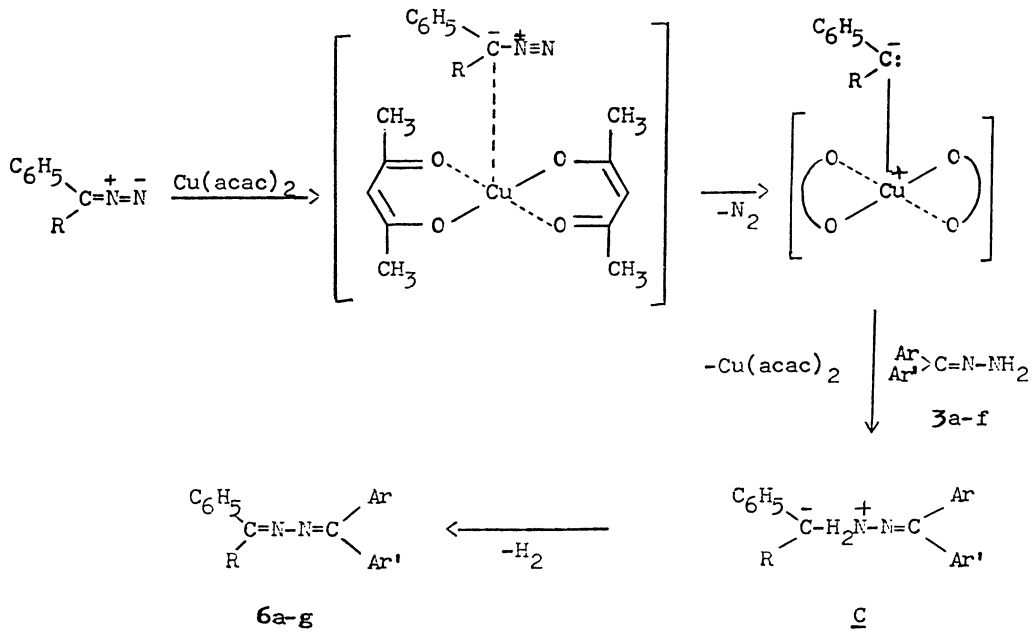
Thermal decomposition of **1** may lead to benzoylphenylcarbene which has been known to undergo Wolff rearrangement to give diphenylketene[12] (Scheme 1). The products **4a**—**c** arise through a proton transfer from the zwitterionic intermediate **A**, formed by the addition of diphenylketene to hydrazones **3a**—**c**. A similar zwitterionic intermediate has been proposed earlier in the reaction of diphenylketene with *N*-benzylideneaniline to give *N*-phenylimidate.[13] Addition of a second molecule of diphenylketene to compounds **4a**—**c** gives rise to products **5a**—**c** through a proton transfer from an intermediate **B**. A similar intermediate has been proposed earlier in the reaction of benzenediazonium ion with aldehyde arylhydrazones to give bis(arylazo)methanes.[14]

The proton shift in **B** appears to be more feasible than the cyclization to β-lactams due to steric factors (pre-



	Ar	Ar′
3a	C_6H_5	C_6H_5
3b	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$
3c	*p*-ClC_6H_4	C_6H_5

Scheme 1.



Scheme 2.

	R	Ar	Ar′	Yield/%
6a	COC_6H_5	C_6H_5	C_6H_5	88
6b	COC_6H_5	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	52
6c	COC_6H_5	*p*-ClC_6H_4	C_6H_5	55
6d	COC_6H_5	C_6H_5	COC_6H_5	92
6e	COC_6H_5	*p*-$CH_3OC_6H_4$	$COC_6H_4OCH_3$(*p*-)	71
6f	COC_6H_5	*p*-$CH_3C_6H_4$	$COC_6H_4CH_3$(*p*-)	85
6g	C_6H_5	C_6H_5	C_6H_5	60

sence of four bulky aryl groups on the terminal carbon atoms in **B**). However, in the presence of bis(acetylacetonato)copper(II), the Wolff rearrangement of the carbene is prevented[4] (Scheme 2) and in this case a carbene–copper complex is formed.[15] The respective carbenes from the complexes react with ketohydrazones to give ketazines **6a**—**g** through an intermediate **C**, formed by the interaction of carbenes with N–H bond of hydrazones.

Experimental

Melting points have been determined on a Büchi apparatus (capillary method) and are uncorrected. The ultraviolet spectra were obtained in 95% ethanol on a Carry-14 spectrophotometer. The infrared spectra were recorded in nujol mull on a Perkin-Elmer 720 spectrophotometer. The PMR spectral data were obtained on a Varian A-60D spectrometer in $CDCl_3$ using TMS as internal standard.

Materials. Benzil, 4,4-dimethoxybenzil, 4,4′-dimethylbenzil, and bis(acetylacetonato)copper(II) were obtained from EGA chemicals, West Germany; benzophenones and hydrazine hydrate from BDH, India; 2-diazo-1,2-diphenylethanone,[16] diphenyldiazomethane,[17] benzophenone hydrazones,[18] and benzil monohydrazones[19] were prepared according to reported methods and characterised on the basis of their analyses and spectral data.

*Preparation of Benzophenone (Diphenylacetyl)hydrazones **4a**—**c**. General Procedure*: A mixture containing 2-diazo-1,2-diphenylethanone (**1**) (0.01 mol) and hydrazones **3a**—**c** (0.01 mol) in 80 ml of dry benzene (thiophene free) in a 250 ml three necked round bottomed flask equipped with a condenser and a mercury trap was heated to reflux for 8 h under a stream of nitrogen and kept overnight at room temperature. The solvent was removed on a rotatory evaporator and residual material was triturated with ethanol. The solid obtained was recrystallized from ethanol to afford the products.

*Benzophenone (Diphenylacetyl)hydrazone (**4a**).* A yield of 80% was obtained, mp 149 °C. UV (EtOH): 290 nm; IR (Nujol): 3325 (N–H); 1690 (C=O) and 1605 cm^{-1} (C=N); NMR ($CDCl_3$) δ=8.85 (s, 1H, NH, D_2O exchangeable), 7.33 (m, 20H, aromatic protons) and 6.17 (s, 1H, CH). Found: C, 82.82; H, 5.84; N, 6.85%. Calcd for $C_{27}H_{22}N_2O$: C, 83.08; H, 5.64; N, 7.18%.

*4,4′-Dimethoxybenzophenone (Diphenylacetyl)hydrazone (**4b**).* A yield of 53% was obtained, mp 119 °C. UV (EtOH): 298 nm; IR (Nujol): 3280 (N–H); 1660 (C=O) and 1605 cm^{-1} (C=N); NMR ($CDCl_3$) δ=9.38 (s, 1H, NH, D_2O exchangeable), 7.33 (m, 18H, aromatic protons), 6.25 (s, 1H, CH) and 3.83 and 3.78 (a pair of singlet, 6H, two OCH_3 protons). Found: C, 77.27; H, 5.91; N, 6.36%. Calcd for $C_{29}H_{26}N_2O_3$: C, 77.31; H, 5.77; N, 6.22%.

*4-Chlorobenzophenone (Diphenylacetyl)hydrazone (**4c**).* A yield of 52% was obtained, mp 99 °C. UV (EtOH): 290 nm; IR (Nujol): 3280 (N–H): 1660 (C=O) and 1600 cm^{-1} (C=N); NMR ($CDCl_3$) δ=8.08 (s, 1H, NH, D_2O exchangeable), 7.20 (m, 19H, aromatic protons) and 6.00 (s, 1H, CH). Found: C, 76.10; H, 5.07; N, 6.66%. Calcd for $C_{27}H_{21}N_2OCl$: C, 76.32; H, 4.94; N, 6.59%.

*Preparation of 1-Diphenylacetylazo-1,1-diaryl-3,3-diphenylpropanones **5a**—**c**. General Procedure*: A similar procedure was used as described above for the preparation of **4a**—**c** taking 0.01 mol of **1** and 0.01 mol of **4a**—**c**.

*1-Diphenylacetylazo-1,1,3,3-teraphenyl-2-propanone (**5a**).* A yield of 71% was obtained, mp 177 °C. UV (EtOH): 250 nm; IR (Nujol): 1670 (C=O) and 1600 cm^{-1} (N=N); NMR ($CDCl_3$) δ=7.40 (m, 30H, aromatic protons), 5.83 (s, 1H, –CHCON=N) and 5.12 (s, 1H, CHCOC). Found: C, 83.87; H, 5.31; N, 5.02%. Calcd for $C_{41}H_{32}N_2O_2$: C, 84.25; H, 5.48; N, 4.79%.

*1-Diphenylacetylazo-1,1-bis(4-methoxyphenyl)-3,3-diphenyl-2-propanone (**5b**).* A yield of 50% was obtained, mp 140 °C. UV (EtOH): 238 nm; IR (Nujol): 1665 (C=O) and 1600 cm^{-1} (N=N); NMR ($CDCl_3$) δ=6.70 (m, 28H, aromatic protons), 5.53 (s, 1H, CHCON=N–), 4.83 (s, 1H, CHCOC) and 3.66 (s, 6H, two OCH_3 protons). Found: C, 80.45; H, 5.90; N, 4.29%. Calcd for $C_{43}H_{36}N_2O_4$: C, 80.12; H, 5.59; N, 4.34%.

*1-Diphenylacetylazo-1-(4-chlorophenyl)-1,3,3-triphenyl-2-propanone (**5c**).* A yield of 51% was obtained, mp 148 °C. UV (EtOH); 248 nm; IR (Nujol): 1670 (C=O) and 1600 cm^{-1} (N=N); NMR ($CDCl_3$) δ=7.20 (m, 29H, aromatic protons), 5.76 (s, 1H, $CHCON_2$) and 5.01 (s, 1H, CHCOC). Found: C, 79.58; H, 5.04; N, 4.26%. Calcd for $C_{41}H_{31}N_2O_2Cl$: C, 79.54; H, 5.01; N, 4.52%.

*Preparation of 1-Diphenylacetylazo-1,1,3,3-tetraphenyl-2-propanone (**5a**) from **1** and **3a**.* A yield of 52% was obtained by using a similar procedure as described above by taking **1** and **3a** in 2:1 molecular ratio.

*Preparation of Ketazines **6a**—**g**. General Procedure*: To a suspension containing 1 m mol of bis(acetylacetonato) copper(II) in 30 ml of dry benzene(thiophene free), heated under reflux with stirring in a 250 ml three necked round bottom flask equipped with a condenser and a mercury trap, a solution containing 0.01 mol of **1** and 0.01 mol of the hydrazones **3a**—**f** in 80 ml of dry benzene (thiophene free) was slowly added over a period of 3 h from a pressure equalizing funnel under a stream of nitrogen. The contents were heated to reflux for additional 4—6 h and kept overnight at room temperature. The reaction mixture was passed through a neutral alumina (10 g, 1.2 cm × 10 cm^2) column and the products were eluted with benzene leaving the copper salt in column. The solvent was evaporated under reduced pressure and the residual material was triturated with ethanol to afford the products.

Similar procedure was adopted for the preparation of ketazines **6g** and **6a** by the reaction of diphenyldiazomethane (**2**) with keto hydrazones **3a** and **3d** respectively.

*2-Diphenylmethylene hydrazono-1,2-diphenylethanone (**6a**).* A yield of 88% was obtained, mp 129 °C. UV (EtOH) : 255, 315 nm; IR (Nujol): 1670 (C=O) and 1600 cm^{-1} (C=N–N=C); NMR ($CDCl_3$) δ=8.00 (m, H, aromatic protons) and 7.38 (m, H, aromatic protons). Found: C, 83.62; H, 4.92; N, 7.39%. Calcd for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21%.

*2-[Bis(4-methoxyphenyl)methylenehydrazono]-1,2-diphenylethanone (**6b**).* A yield of 52% was obtained, mp 95 °C. UV (EtOH): 252, 295 nm; IR (Nujol): 1670 (C=O) and 1600 cm^{-1} (C=N–N=C); NMR ($CDCl_3$) δ=8.10 (m, 2H, aromatic protons), 7.30 (m, 16H, aromatic protons) and 3.96 and 3.81 (two s, 6H, two OCH_3 protons). Found: C, 77.60; H, 4.97; N, 6.14%. Calcd for $C_{29}H_{24}N_2O_3$: C, 77.67; H, 5.34; N, 6.25%.

*2-(4-Chloro-α-phenylbenzylidenehydrazono)-1,2-diphenylethanone (**6c**).* A yield of 55% was obtained, mp 114 °C. UV (EtOH): 255, 315 nm; IR (Nujol): 1670 (C=O) and 1600 cm^{-1} (C=N–N=C); NMR ($CDCl_3$) δ=7.66 (m, H, aromatic protons) and 7.13 (m, H, aromatic protons). Found: C, 76.80; H, 4.75; N, 6.79%. Calcd for $C_{27}H_{19}N_2OCl$: C, 76.68; H, 4.49; N, 6.62%.

*2-(α-Benzoylbenzylidenehydrazono)-1,2-diphenylethanone (**6d**).* A yield of 92% was obtained, mp 201 °C. UV (EtOH): 255, 315 nm; IR (Nujol): 1680 (C=O) and 1601 cm^{-1} (C=

N–N=C); NMR ($CDCl_3$) δ=7.99 (m, H, aromatic protons) and 7.45 (m, H, aromatic protons). Found: C, 80.76; H, 4.86; N, 6.79%. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.76; H, 4.80; N, 6.73%.

*2-[4-Methoxy-α-(4-methoxybenzoyl)benzylidene hydrazono]-1,2-diphenyl-ethanone (**6e**).* A yield of 71% was obtained, mp 131 °C. UV (EtOH): 255, 320 nm; IR (Nujol): 1660 (C=O) and 1601 cm^{-1} (C=N–N=C); NMR ($CDCl_3$) δ=7.92 (m, 4H, aromatic protons), 7.13 (m, 14H, aromatic protons) and 3.83 and 3.72 (two s, 6H, two OCH_3 protons) Found: C, 75.54; H, 5.10; N, 6.03%. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.62; H, 5.08; N, 5.88%.

*2-[4-Methyl-α-(4-methylbenzoyl)benzylidenehydrazone]-1,2-diphenylethanone (**6f**).* A yield of 85% was obtained, mp 151 °C. UV (EtOH): 255, 320 nm; IR (Nujol): 1670 (C=O) and 1601 cm^{-1} (C=N–N=C): NMR ($CDCl_3$) δ=7.90 (m, 4H, aromatic protons), 7.25 (m, 14H, aromatic protons), and 2.33 and 2.20 (two s, 6H, two CH_3 protons). Found: C, 81.10; H, 5.46; N, 6.22%. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30%.

*Benzophenone azine (**6g**).* A yield of 60% was obtained, mp 161 °C. UV (EtOH): 275, 310 nm; IR (Nujol): 1600 cm^{-1} (C=N–N=C); NMR ($CDCl_3$) δ=7.33 (m, H, aromatic protons). Found: C, 86.58; H, 5.49; N, 7.75%. Calcd for $C_{26}H_{20}N_2$: C, 86.66; H, 5.56; N, 7.78%.

*2-Diphenylmethylene hydrazono-1,2-diphenylethanone (**6a**).* A yield of 75% was obtained in the reaction of **2** with ketohydrazone **3d**, mp 129 °C, mmp 129 °C. The IR spectrum was superimposable to that of the product described above.

We are thankful to Professor B. M. Shukla for providing the facilities and to C. S. I. R., New Delhi, for grant of a fellowship to G. S. S.

References

1) S. B. Singh and K. N. Mehrotra, *Can. J. Chem.*, **59**, 2475 (1981).
2) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).
3) J. L. E. Erickson, J. M. Dechary, and M. R. Kesling, *J. Am. Chem. Soc.*, **73**, 5301 (1951).
4) M. Takebayashi, T. Ibata, H. Kohara, and B. H. Kim, *Bull. Chem. Soc. Jpn.*, **40**, 2392 (1967).
5) K. N. Mehrotra and G. S. Singh, *Indian J. Chem., Sect.B*, **21**, 672 (1982).
6) S. B. Singh and K. N. Mehrotra, *Bull. Chem. Soc. Jpn.*, **54**, 1838 (1981).
7) E. Fahr, K. Doppert, and Konigsdorfer, *Tetrahedron*, **23**, 1379 (1967).
8) S. B. Singh and K. N. Mehrotra, *Can. J. Chem.*, **60**, 1901 (1982).
9) K. N. Mehrotra, S. B. Singh, and K. N. Singh, *Indian J. Chem., Sect.B*, **21**, 146 (1982).
10) O. Gerhardt and H. Bodenkueture, *Monatsh*, **41**, 199 (1920); *Chem. Abstr.* **14**, 3409 f (1920).
11) D. B. Mobbs and H. Suschetzky, *J. Chem. Soc., C.* **1971**, 175.
12) V. Frangen, *Ann.*, **614**, 31 (1958).
13) W. Jugelt and D. Schmidt, *Tetrahedron*, **25**, 969 (1969).
14) A. F. Hegarty, "*The Chemistry of Hydrazo, Azo and Azoxy Groups*", ed by S. Patai, Interscience, New York (1975), Vol. II, p. 669.
15) H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).
16) C. D. Nenitzescu and E. Solomonica, *Org. Synth.*, Coll. Vol. II, 496 (1950).
17) M. Fieser and E. Fieser, "*Reagent for Organic Synthesis*," John Willey, & Sons New York (1966), Vol. I, p. 338.
18) R. Baltzly, R. B. Mehta, P. B. Russel, R.E. Brooks, E. M. Grivsky, and A. M. Steinberg, *J. Org. Chem.*, **26**, 3669 (1961).
19) L. I. Smith and H. H. Hoehn, *Org. Synth.*, Coll. Vol. III, 356 (1955).