Pak j. sci. ind. res., vol. 37, no.12, December 1994

CONDENSATION REACTIONS OF 1, 3-DIPHENYL-2-PROPEN-1-ONES WITH NUCLEOPHILIC REAGENTS

A.U. Rehman and M.A. Qureshi

Department of Organic and Natural Products, Institute of Chemistry,

University of Sindh, Jamshoro, Pakistan

(Received May 4, 1994 ; revised November 6, 1994)

The reactivity of substituted 1,3-diphenyl-2-propen-1- ones has been investigated under acidic and basic conditions with amino-compounds resulting to heterocyclic derivatives. Other reactions with ethyl acetoacetate and acetylacetone have afforded substituted 3,5-disphenylcyclohexenones.

Key words: Condensation of 1,3-propenones, Amino and β-Ketonic Compounds.

Introduction

Compounds containing -N-C-S-grouping such as thiazoline thiazole, thiazine etc. have been reported to possess medicinal properties [1-5]. The other class of compound containing -N-C-N-grouping also possess biological properties, some pyrimidine analogues bear the metabolic inhibitor character and plays the vital role of anticancer agents [6-8].

The substituted 1,3-diphenyl-2-propen-1-ones reacts with hydroxylamine hydrochloride to form β–τ- unsaturated ketoximes [9-11] which undergoes a variety of reactions, cyclization catalytic hydrogenation and Beckmann rearrangements [12-14]. Pyrozoline are also formed by the reaction of Chalcones with hydrazine hydrate, such reactions are repoted in the literature [12,15]. The concept when extended to substrates which have a double bond Juxtaposition to the carbonyl group has opened the ways to form a variety of compounds [17]. The interaction of double bond and a carbonyl function, encourages, conjugate 1,4-addition of nucleophilic reagent and is possible in both acidic and basic catalytic pathways, to accomplish cyclic ones. The products were chromatographically purified and analyzed various functional group frequencies observed in the infrared spectra. They were further rationalized π-π* transition function, like - C=N, -C=C- and - C=O in the ultraviolet absorptions presents in the required structures. The structures of few compounds were determined on the ^{1}H-nmr parameters.

Experimental

All melting points were determined on digital Gallenkemp melting point apparatus and are uncorrected infrared spectra were recorded on SP 1024 Pye Unicam spectrophotometer, ultraviolet, absorption spectra were determined using ethanol and methanol (spectroscopic grade).

2-0xo-4- (o'-hydroxyphenyl)-6- (p'-methoxyphenyl) -3, 6-dihydro- 1,3- thiazine (2a). 1-(o-hydroxyphenyl)-3-(p-methoxyphenyl) -2- propen-1-one (la) (2.69 g, 0.01 mole) and thiourea (3.04, 0.04 mole) were dissolved in ethanol (50 ml). Diluted sulfuric acid (8 ml, 6N) was added to the reaction mixture and the flask was heated for 6-8 hrs on a steam bath. The reaction mixture was cooled, the solvent was evaporated, and the residue was washed repeatedly with hot water to remove the unreacted thiocarbamide. The solid obtained was dissolved in diethyl ether and the etheral solution washed with water, then dried (sodium sulfate), concentrated and subjected for further purification by column chromatography using benzene and methanol (25.1 v/v). The fraction after concentration have afforded a yellow crystal of (2a) m.p 85° - 87° in 85% yield. IR: 3350 (-NH str.), 3245 (-NH) 3030 (=CH, aromatic), 1640, 1580, 1560 (C=C, phenyl ring vibration), 1615 (C:O-NH, Str. vibrations 1450 cm^{-1} (CH. def. in CH_2). UV: 254, 271, 294, 314 nm (ethanol):

(Found: C, 65.15; H, 4.34; N, 4.41% Calcd for $C_{17}H_{14}NO_3S$ C, 65.38; H, 4.51; N, 4.48%).

1,3-(o-chloro) diphenyl-2-propen-1-one (1b) (2.42 g, 0.01 mole was used for the synthesis of *2-oxo-4-(o-chlorophenyl)-6- phenyl -3,6-dihydro-1, 3-thiazine* (2b) m.p. 141-2°, in 70% yield, IR 3345 (-NH, Str.), 3030 (=CH, aromatic Str.) 1640, 1575, 1560 (C=C, phenyl ring vib.) and 1618 cm^{-1} C:O-NH). UV: 220, 260, 284, 314 nm (ethanol): (Found, C, 63.51: H, 4.10, N, 4.60% Calcd, for $C_{16}H_{12}NOSCl$: C, 63.68, H, 4.00, N, 4.63%).

2-Oxo-4-(o'-hydroxyphenyl)-6-(p-methoxyphenyl)-1, 3, 6-trihydro-pyrimidine (2a) was obtained by the treatment of compound (1a) (2.69 g, 0.01 mole) and carbamide (2.4 g, 0.04 mole) in ethanol (50 ml) and diluted sulfuric acid 10 ml (6N): After work up, gave crystalline compound (3a) m.p. 120-21°C

in quantitative yield IR: 3450, 3250 (-NH, str. vib), 3015(=CH aromatic 1460 (-CH_2 gr), 2910 (-CH_2-Sym, str. vib) 1650, and 1655 (C=C, str. aromatic ring), 17.50 and 1710 (C=0.gr) 1310 cm^{-1} (CH-def). UV: 274, 291, 315, 340 nm (methanol). (Found: C, 68.71; 5.55, N, 9.40% Calcd for $C_{17}H_{16}N_2O_3$ C, 68.90, H, 5.44, N, 9.44%).

2-Oxo-4-(o-chlorophenyl)-6-phenyl-1,3,6,-trihydropyrimidine (3b) was obtained in 74% yield m.p. 185-186°, IR: 3450, 3250 (-NH) 3030 (=CH, phenyl gr. vib.) 2910 (-CH_2-gr sym str. vib.) 1575, 1645, 1665, (C=C, phenyl gr. vib), 1715cm^{-1} (C=O, gr. str.). (Found: C, 67.41; H, 4.51; N, 9.91% Calcd for $C_{16}H_{13}N_2OCl$, C, 67.48, H, 4.60, N, 9.83%).

2-Amino-4-(o-hydroxyphenyl)-6-(p-methoxyphenyl) 3,6-dihydro pyrimidine (4.a). To a solution of (1.0 g, 0.001 mole) of quanidine hydrochloride and (compound (1 a) (2.69 g, 0.01 mole) in ethanol (50 ml) was added potassium hyroxide (2.8 g, 0,050 mole) in 25 ml of ethanol. The resulting mixture was heated under reflux on a steam bath for 4 hrs. The precipitates which formed when the reaction was cooled, was thoroughly washed with warm water to remove any inorganic salt, and then with warm alcohol. After drying the crystals, under P_2O_5 desicant, the crystals m.p. 158-9° in 87% yield.

IR: 3510 (-NH_2 Str. Vib.), 3350 (-NH, gr),3015 (=CH Str. vib of phenyl gr), 2920, (-CH_2 Sym. Str. Vib), 1630, 1650, 1665 (C=C, phenyl gr vibrations). UV: 235, 275, 310, 318 (ethanol) (Found C, 69.10; H, 5.75, N, 14.11% Calcd. for $C_{17}H_{17}N_3O_2$ C, 69.13; H, 5.80, N. 14.22%). Similarly, *2-amino-4-(0-chlorophenyl) -6-phenyl-3, 6-dihydropyridine (4b),* was obtained in 62% yield as crystalline product m.p. 155-6°C. The vibrations in the infrared spectrum and the ultra violet absorptions are in conformity with the structure; (Found C, 67.51, H, 4.95, N, 14.55% Calcd, for $C_{16}H_{14}N_3Cl$, C, 67.76; H, 4.97: N, 14.80%).

4-(O-hydroxyphenyl)-6-(p-methoxyphenyl)-2, 5-dihydro-isoxazole (5). A solution of compound (1a) (2.69 g, 0.01 mole) and hydroxylamine hydrochloride (1.4 g, 0.02 mole) in dry pyridine (15 ml) was heated on a steam bath for 2-3 hrs. The oily product obtained on adding excess of water, crystallized from methanol to yield the desired compound (5) yellow crystals, m.p. 232-3° in 52% yield. IR: 3350 (NH, Str.) 3010 (=CH, Str. Vib.) 2910 (-CH_2 gr). 1650, 1665 cm^{-1}, (C=C, phenyl gr. vib.) UV: 245, 265, 310 (methanol) (Found: C, 71.13; H, 5.45, N, 5.11% Calcd for $C_{16}H_{15}NO_3$ C, 71.36; H, 5.61; N, 5.19%).

Acetylation was carried out under the conventional procedure, the mixture was heated and work up as usual. It gave an oil product, which could not be triturated with common solvents. The oil was column chromatographed (silica-gel), eluted with benzene-methanol chloroform 25:1:5: v/v. The fractions after evaporation gave a crystalline product, m.p. 145-6°, IR: 3021 (=CH, Str. in aromatic), 2950 (CH-Str in CH_2 1715 (C=O Str) 1610 and 1516 (C=CH aromatic) 1370 (CH, def), 772 and 695Cm^{-1} (distributed benzene. *3-(O'-hydroxyphenyl)-5-p-methoxyphenyl)-4, 5-dihydroisoxazole (6).* In small round bottomed flask (1 g) of compound (5) was poured, and heated above their melting points for 5-10 mins. The oil product was crystallized from methanol, after refrigeration for 24 hrs, this was solidified, filtered off, and the cyrstalline product m.p. 187-8°C IR: 3350 (-NH Str. Vib) 3215 (-NH, sym str. vib) 3010 (=CH, phenyl gr. vib), 2870, 1465, 720 (CH_2) 1640, 1650 cm^{-1} (C=C, aromatic str). The ultraviolet absorptions spectra supports the structure.

3-(O'-hydroxyphenyl)-5-(p-methoxyphenyl)-4, 5-dihydro-pyrazole (7). Compound (1a) (2.7 g), hydrazine hydrat 5 ml, 66%) and pyridine (10 ml) were heated on a steam bath for 2 hrs. The solid obtained on adding water ethanol mixture and left in refrigerator for 24 hrs to give (7) as yellowish red syrup in 75% yield. IR: 3450 (-NH-1), 3360 (-NH-II), 3030 (=CH, phenyl ring vib), 2950 (-CH_2- Str. vib), 1650, 1665 cm^{-1} (C=C-phenyl ring streteching. UV: 265, 295, 315, 330, 345 nm (methanol).

(Found C, 71.31, H, 6.15, N, 10.29% Calcd for $C_{16}H_{16}N_2O$: C, 71.62, H. 6.01, N, 1043%).

The N-acetyl derivative of (7) was prepared and recrystallized from methanol. The crystals melts at 195-6°, ^1H NMR: δ 3H, s, 2.30, 2H m, 3.50, 3.65 3H, 3.75, 1H, dd, 5.75, J = 10.0 4H. m, 6.65-7.30 2H, d, 7.82, J=10.5 Hz.

1-Phenyl-3-(o-hydroxyphenyl)-5-(p-methoxyphenyl)-pyrazoline (8a). In a solution of compound (1a, 2.67 g), was added phenylhydrazine (1.5 g, 0.15 mole) in glacial acetic acid (5 ml) and ethanol (20 ml) with efficient stirring at room temperature for 5 hrs. After stirring crystallization begins and completed within 30 mins.

This was heated under reflux for 1 hr, this process bring up the total rearrangement to the isomeric pyrazoline in a crystalline product. The traces of acetic acid were removed by washing several times with cold alcohol, eventually affored a crystalline product m.p. 151-152°: The bends present in infrared spectrum shows the various functional group involved in the structure.

Similarly, compound (1b) (2.42 g, 0.01 mole) was treated with phenyl hydrazine in equimolar ratio,gave *1,5-diphenyl-3-(o'-chlorophenyl) pyrazoline (8b) in quantitative* yield, m.p. 120-121° , IR: 3350, 3245 (-NH gr str.) 3050 (=CH phenyl gr.vib.) 2925 (-CH_2-Sym. Str.) 1650, 1665, 1575 cm^{-1} (CH=CH phenyl gr. vibrations). (Found C, 75.67; H, 5.42, N, 8.30% Calcd. for $C_{21}H_{17}N_2Cl$, C, 75.77, H, 5.14, N, 8.41%).

1-(2'-nitrophenyl)-3-(hydroxyphenyl)-5-(p-methoxyphenyl) pyrazoline (9) was obtained by the treatment of 2-nitrophenyl hydrazine (2.23 g, 0.015 mole) in glacial

acetic acid (5 ml) and then mixed with compound (1 a) in 25 ml of ethanol. This was heated under reflux for 30 mins on a steam bath, then cooled and filtered off the solid, washed several time with ice-cold water. This was later washed with cold ethanol, finally yielding 47% of the required product m.p. 233-4°C.

The infrared and ultraviolet absorption bands have supported the structure. (Found C, 74.51, H, 5.21; N, 10.54% Calcd. for $C_{22}H_{20}O_4N_3$ C, 74.75: H, 5.61; N, 10.75%).

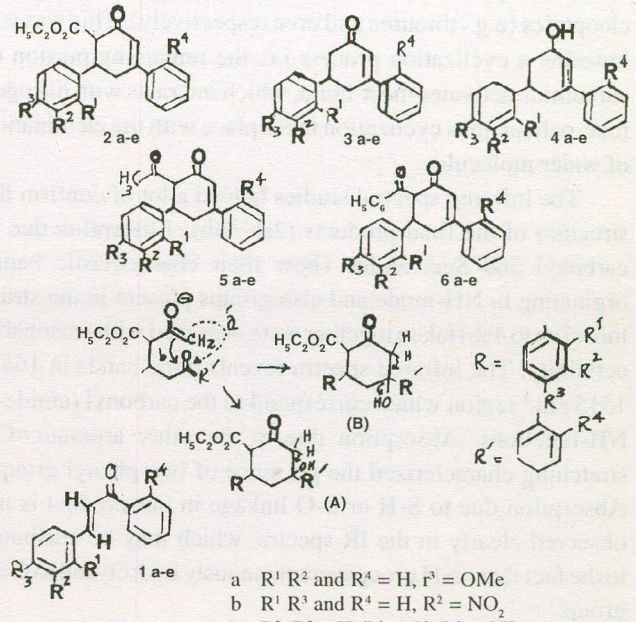
2-Carbethoxy-3-(o-hydroxyphenyl)-5-(p-methoxyphenyl) cyclohexenone (10a). Freshly distilled ethylacetoacetate (6.0g, 0.05 mole) was added to an alcoholic solution of sodium ethoxide that had been prepared from sodium (0.013 g atom) and 140 ml of absolute ethyl alcohol. After stirring the reaction mixture for 1 hr. The compound (1 a) (2.8 g, 0.011 mole) was added and resulting solution was refluxed for 4 hrs. The solution while hot was added to cold dilute hydrochloric acid (1N, 15 ml). A yellow precipitate was isolated by suction filtration and recrystallization from 95% ethanol to a yellowish white solid. m.p. 146-7° in 47% yield. IR: 1740 (ester C=0) and 1665 cm^{-1} (C=0), UV: 235, 265, 280 in (ethanol) (Found C, 72.41, H, 6.15% Calcd. for $C_{22}H_{22}O_5$ C, 72.11, H, 6.05%).

3-(O'-Hydroxyphenyl)-5-(p-methoxy-phenyl) cyclohexenone (11a). The ketoester (10 a) (3.6 g, 0.01 mole) was added to a solution containing sodium hydroxide (2.4 g) dissolved in a mixture of 50 ml of ethanol and 20 ml of water. The mixture was refluxed for 3 hrs, cooled and extracted with benzene. The benzene layer was washed with water and dried. The benzene was evaporated and a yellow oil was obtained which was crystallized from ethanol to give white solid. m.p.° 118-119°), 85% yield. IR: 3015 (=CH, aromatic), 2950 (-CH_2- Str.), 1650 (C=O) 1685 1665, 1645cm^{-1} (C=C) phenyl gr.vib). UV: 270, 230, 225, nm (methanol):

2-carbethoxy-3-(o-chlorophenyl)-5-phenylcyclohexenone (10 b) was obtained under the prescribed procedure for compound (10 a), had afforded 71% yield (10 b) as a crystalline product m.p. 219-20°. The infrared and absorptions levels in the ultraviolet have supported the structure (Found C, 71. 14, H, 5.31% Calcd for $C_{21}H_{19}O_3Cl$, C, 71.07, H, 5.39%). Allalive hydrolysis and decarboxylation of (10b) gave a white crystalline product m.p. 181-2°C in quantitative yield. IR: 3015 (=CH, aromatic), 2915 (-CH_2- gr.) 1660 (C=O), 1674, 1655, 1645 cm^{-1} (=CH, phenyl gr. vibrations), UV 254, 225, nm (methanol).

2-Acetyl-3-(o'-hydroxyphenyl)-5-(p-methoxyphenyl) cyclohexenone (12 a) was obtained by the treatment of acetylacetone (1.25 g, 0.01 mole) and compound (1a) (2.8 g) in alcoholic sodium ethoxide (50 ml). This was worked up as mentioned above finally afforded the required compound (11a) as a thick syrup in 63% yield. The IR an UV parameters are in confirmity with the structure (Found C, 74.39; H, 6.20, Calcd for $C_{21}H_{21}O_4$: C, 74.75; H, 6.27%).

Similarly, *2-acetyl-3-(o-chlorophenyl)-5-phenyl cyclohexenone (12b)* was synthesized from compound (1b) as crystalline product m.p. 185-186 in quantitative yield: IR=3015 (=CH, aromatic), 2950 (CH_2), 1650 (C=O), 1690, 1884 and 1665 (CH=CH-CO, gr.) 980 and 780 cm^{-1} (CH, deform. vib). Found C, 73.65, H, 5.41, Calcd for $C_{20}H_{18}O_2Cl$ C, 73.71, H, 5.56%).



a R^1 R^2 and R^4 = H, r^3 = OMe
b R^1 R^3 and R^4 = H, R^2 = NO_2
c R^2, R^3 = H, R^1 = Cl, R^4 = OH
d R^1 and R^2 = H, R^3 = $N(CH_3)_2$, R^4 = OH
e R^1, R^2 and R^4 = H, R^3 = $N(CH_3)_2$

Result and Discussion

H.O. House [17] has suggested that carbon ions with little or no resonance stabilization give 1,2-addition whereas stabilized carbon ion [18] of the type R-CR=CH C-R tends to give 1,4-addition products. The principle of the addition reaction is still the same, but the mechanism varies a bit. Both acid and base catalyzed pathways are available and which one is prefered depend on the nature of substrates and reagents used.

1,4-Conjugated oxidation product 2-oxo-4, 6-diphenyl-3, 6-dihdyro-1, 3-thiazine (2-ab) was obtained as crystalline product from 1,3-(o-chloro) diphenyl-2-propen-1-one (1a) and 1-(o'- hydroxyphenyl)-3-(p-methoxyphenyl)-2-propen-1-one (1b), with thiourea using dilute sulfuric acid [19,20]. The compound (1 ab) when treated with urea under acid catalyst, after brief refluxing yield, 2-oxo-4,6-diphenyl-1,3,6-trihydropyrimidine (3 ab) as crystalline products. Similar be-haviour has been reported for amidine hydrochloride which reacts with R-CH=CH-COR type of ketone to yield the

cycloaddition products i.e. substituted pyrimidines in quantitative yields. We also adopted similar procedure during the reaction between guanidine hydrochloride with above ketones (1-ab) to give various yields of 2-amino-4,6- diphenyl-3, 6-dihydropyrimidine. (4-ab) in an alcoholic solution of potassium hydroxide.

The mechanism of the above reactions presumably, the initial protonation of the carbonyl group of the α, β-unsatureated ketone leads to the migration of π-electron thereby generating a carbonation at the β-position, which is attached by the lone pair electrons of sulfur and nitrogen from the nucleophiles (e.g., thiourea and urea respectively). This was followedby a cyclization process i.e. the remaining portion of carbamide activates the π-bond, which interacts with nitrogen lone-pair, an thus cyclization takes place with the elemination of water molecule.

The infrared spectral studies helped a lot of confirm the structure of the final products (2ab-4ab). Absorption due to carbonyl and Sec. amide show their characteristic bands orginating in NH-mode and also groups present in the structure (2ab to 4ab) taken together were observed with reasonable certainity. The infrared spectra reveals three bands in 1645-1515 cm^{-1} region which correspond to the carbonyl (amide-I) NH-functions. Absorption due to the other aromatic=CH stretching characterized the presence of two phenyl groups. Absorption due to S-H or S-O linkage in our product is not observed clearly in the IR spectra, which may be attributed to the fact that =NH group instantaneously hydrolyzed to C=O group.

The ultra violet showed absorption band characteristic to phenyl and C=ONH groups. The bathochromic shift in these bands may be explained due to participation of olefinic bonds with phenyl rings. Absorptions ca 275 nm is due to heterocyclic ring containing -CONH functions.

When 1,3-diphenyl-2-propen-1-ones (1 ab) was warmed with hydroxylamine hydrochloride in pyridine, it gave good yields of yellowish crystals of the required 3,5-diphenyl 2,5-dihydro isoxazole (5) and shows blue colour to gibb's reagent [21]. The product when heated above their melting point, rearranges to a lower melting 3,5-diphenyl-4, 5-dihydroisoxazole (6). They are apparently identical with the above products obtained by prolong heating of compounds (1 ab) with hyroxylamine hydrochloride in pyridine.

The ^1H nmr spectrum of the compound (5) closely coincide with that of 3,5-diphenyl 4,5-dihydroisoxazole ring appears as well as HA, HB and HC proton as well defined doublets at δ3.41, 3.58 and 5.61 respectively with J_{AB}=16.0Hz J_{AC}, 8.0; J_{BC}=10.0 Hz.

Hydrazine hydrate also reacts with compound (1 ab) to give 3, 5-diphenyl-4, 5-dihyropyrazoles (7). These compounds form oily diacetylderivatives on treatment with acetic anhydride and pyridine. The ^1H nmr parameter show the presence of HA HB and HC protons appearing as double doublets at 3.00, 3.51, and 4.65 respectively. Assignments of C=C and C=N double bonds in the given 2,5- and 4,5-dihydroisoazole compounds have been achieved by infrared and ultraviolet absorption maxima.

The specific character of 1,3-diphenyl-2-propen-1-one (1 ab) when treated with phenyl hydrazine and ortho-nitro substituted analogye in acetic acid medium to yield the corresponding phenyl hydrazones. They are on brief refluxing readily cyclizing to desired 1,3, 5-triphenylpyrazolines (8 ab) and (9). The infrared and ultraviolet data are in confirmity with the structures (8 ab) and (9).

In the literature [22], the preparation of linear m-polyphenyl cyclohexenones (i. e. 3, 5-disubstituted) has been achieved, by employing the reaction of 3-ethoxy-2-cyclohexenone with organolithium or Grignard reagents. The character of radicals in an α, β-unsaturated ketone, of the type R-CH=CH-CO-R sources as a starting material for the synthesis of m-polyphenyl system [23]. During the transformation sequence it undergoes a base catalyzed aldol condensation, followed by dehydration to desired 3,5-diphenylcyclohexenone, which aromatized to corresponding m-polyphenyl products.

The Michael condensation of freshly distilled ethylacetoacetate with starting meterial (1 ab) in presence of sodium ethoxide in ethanol afforded various yields of 2-carbethoxy 3,5-diphenylcyclohexenone (10 ab). During refluxing, the aldol products formed dehydrated leading to 2-carbethoxycyclohexenone product (II ab). The decarbooxylation was observed under either basic or acidic conditions. Hydrolysis and decarboxylation was achieved by alkaline conditions to give better results.

On refluxing the carbon ion of β-diketone (acetylacetone) interacts with the cationic carbon to compounds (1 ab) and led to the formation of a new carbon-carbon bond. This was followed by cyclization, which involves the dehydration to corresponding α, β-cyclicenones (12 ab) in good yields. Main features of the infrared spectra of these compounds is lowering of the carbonyl group stretching frequencies as it is a part of the conjugated system. Various other functional group frequencies are observed in the given spectra that helps in the confirmation of the given structures.

References

1. R. Kuhn and F. Drawert, Ger. Pat., 937231, Chem. Abstr., 8248h.49 (1955).
2. G. R. Handrick, E. R. Aleinson, F. E. Granchelli and R. J. Brouni, J. Med. Pharm. Chem., **8,** 762 (1965).

3. G. H. Mizzoni and P. C. Elsman, J. Am. Chem. Soc., **80,** 3470 (1958).
4. T. Bachelli, U. S. Pat., 2784196 (1957), Chem. Abstr., 129821g, 51 (1957).
5. J. R. Geigy, Fr. Pat., 1395069 (1965), Chem. Abstr., 4301d, 63 (1965).
6. G. H. Hitching and G. B. Elion, *Purine Analogues,* Metabolic Inhibitors (Eds), R. M. Hocheter, and J. H. Quastel (Academic Press, New York, 1963), Vol.1, pp.215.
7. R.W. Brockmann and E.P. Anderson *Pyrimidine Analogues* Metabolic Inhibitors (Eds) R.M. Hochster and J.H. Quastel (Academic Press, New York, 1963), Vol. I, pp. 215.
8. R. W. Bruckman, Adv., Cancer Res. **7,** 129 (1963).
9. K. V. Auwers and H. Muller, J. Prockt Chem., **137,** 57 (1933).
10. J. Meisenheimer and N. Campbell, Annalen, **539,** 93 (1939).
11. K. Samula, Roczniki, Chem., **45,** 2063 (1971).
12. A. Dornow and A. Ferse, Arch. Pharm, **285,** 463 (1952).
13. V. E. Ruchkin, E. Shversoka, K. D. Shilovskaya and N. N. Melnikov, Proble, Poluch, Poluproa, Prom Org. Syn Akad. Nauk. SSR Otd. Obshch, Tekh Klim, 66 (1967), Chem. Abstr., 95417g, 68 (1968).
14. S. Lenka, P. L. Nayak and M. K. Rout, J. Ind. Chem. Soc., **42,** 162 (1970).
15. C. L. Pederson, N. Henrit and O. Buchardt, Acta, Chim. Scand., **74,** 3455 (1970).
16. A.T.Balaban, Tetrahedron, **24,** 5059 (1969), **26,** 739 (1970).
17. R. E. Gawley, Synthesis, 777 (1976); M.E. June, Tetrahedrons, **32,** 3 (1976) and H.O. House, *Modern Synthetic Reactions* (New York, W.A. Bengomin, Inc. 1965), pp-210-212.
18. E. D. Bergman and D. Ginsburg and R. Pappo, Org. Reaction, **10,** 179 (1959).
19. A. R. Katritzky, A. J. Boulton, *Adv. in Heterocyclic Chemistry* (Academic Press, New York, 1975), Vol.18 pp.100.
20. D. N. Dhar and A. K. Singh, Annual Convention of Chemical Abstr. Org. Chem., **57,** 22 (1976), Indian J. of Chem., **17B**, 25 (1979).
21. L. Jurd, Tetrahedron, **25,** 2367 (1969), F. E. King and T. J. King and C. C. Manning, J. Chem. Soc., 563 (1957).
22. G. F. Woods, F. T. Reeds, T. E. Arthur and H. J. Ezekiel, J. Am. Chem. Soc., **73,** 3854 (1951), G.F. Wood, D. D. Centole, H. E. Ruskie and C. D. MIller, Ibid, **82,** 5227 (1960).
23. N. B. Sunshine and G.F. Woods, J. Org. Chem., **28,** 2517 (1963), **28,** 2514 (1963).