water (3 l.), and finally decomposed with solid sodium carbonate to regenerate the ketone. This was isolated by filtration, washed with water and very dilute acid, dried, and recrystallized from benzene. 5-Phthalimido-2-tetralone, 105 g., 63% yield, was obtained as colorless prisms, m.p. 200–202°. These crystals tenaciously retained traces of the benzene solvent. The analytical sample was recrystallized from a mixture of chloroform and methanol as colorless needles, m.p. 202–204°.

Anal. Calcd. for $C_{18}H_{13}O_3N$: C, 74.21; H, 4.50; N, 4.81. Found: C, 74.48; H, 4.35; N, 4.64.

CHANDLER LABORATORIES
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

---

(4) In this sequence, the period of refluxing for conversion of the phthalamic acid to the phthalimide is not critical, but the time required for cleavage of the enol ether is. The acetic acid solution may be refluxed indefinitely beyond the 2 hour period suggested without impairment of yield. For the aqueous hydrochloric acid treatment, however, the yield of 5-phthalimido-2-tetralone falls off fairly rapidly with periods appreciably more than 2 minutes, and with shorter periods cleavage of the enol ether is not complete.

The Mesomorphic State. Phototropy of *p-n*-Nonoxybenzalphenylhydrazone and *p-n*-Decyloxybenzalphenylhydrazone

GLENN H. BROWN AND WILFRID G. SHAW

Received August 13, 1958

It is well known that a large number of organic compounds are mesomorphic in character. Even though it is not the purpose of this report to emphasize that the phenylhydrazones described here are mesomorphic, it might be mentioned that no phenylhydrazones with this property appear to have been described in the literature previously. An extensive review of the structure and the properties of the mesomorphic state may be found in a recent article by Brown and Shaw.[1]

Phototropic character of a number of both inorganic and organic compounds is also well established. Marckwald[2] gave the name "phototropy" to the phenomenon in which a solid changes color when exposed to light but reverts to its original color in the dark. Chalkley[3] reviewed the subject of phototropy a number of years ago. A number of phenylhydrazones have been described in the literature as phototropic and those described before 1928 are cited in Chalkley's review.[3] Gheorghiu and Matei[4] found the *α*-phenylhydrazones of 1-benzylidene-2-propanone, 1-benzylidene-2-pentanone, and 4-methyl-1-piperonylidene-2-pentanone are all phototropic but these compounds were not described as mesomorphic in character. Matei[5] reported the phototropic character of the *α*-phenylhydrazones of 1-benzylidene-2-butanone and of 1-benzylidene-2-pentanone but they were not described as showing mesomorphism.

The purpose of this preliminary report is to record two compounds which exhibit the properties of both mesomorphism and phototropism. No such compounds appear to have been described in the literature previously.

In the progress of research on the mesomorphic properties of a series of phenylhydrazones, it was found that *p-n*-nonoxybenzalhydrazone and *p-n*-decyloxybenzalphenylhydrazone both exhibit phototropy and mesomorphism. *p-n*-Nonoxybenzalphenylhydrazone has a crystalline-nematic point of 94–95° and a nematic-liquid point at 97–98°. It gives white flakes on crystallization from ethanol; these white flakes turn pink on exposure to direct sunlight. The compound was recrystallized from ethanol until it showed constant transition points.

Anal. Calcd. for $C_{22}H_{30}ON_2$: C, 78.06; H, 8.93. Found: C, 77.86; H, 8.72.

The color change from white to pink is rapid, taking place in less than five minutes. The reverse process, pink to white, takes place in about two hours. *p-n*-Decyloxybenzalphenylhydrazone crystallizes from ethanol to give white flakes which turn red on exposure to sunlight; the reverse process also takes place but is much slower than the rate of excitation. The time change on color transitions for this compound are comparable to those of *p-n*-nonoxybenzalphenylhydrazone. *p-n*-Decyloxybenzalphenylhydrazone has a crystalline-nematic point of 91–92° and a nematic-liquid point of 93–94°. The compound was recrystallized from ethanol until it showed constant transition points.

Anal. Calcd. for $C_{23}H_{32}ON_2$: C, 78.36, H, 9.15. Found: C, 78.11; H, 9.02.

The phototropic process for both compounds can be repeated again and again. No study has been made whether or not the compounds fatigue.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

---

(1) G. H. Brown and W. G. Shaw, *Chem. Revs.*, **57**, 1049 (1957).

(2 W. Marckwald, *Z. physik. chem.*, **30**, 140 (1899).

(3) L. Chalkley, *Chem Revs.*, **6**, 217 (1929).

(4) C. V. Gheorghiu and V. Matei, *Bull. soc. chim. France*, [5] **6**, 1324 (1939).

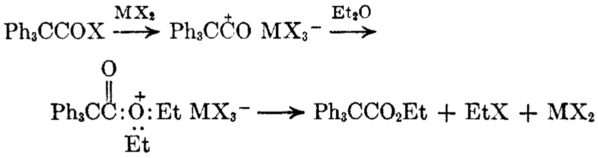
(5) V. Matei, *Ann. sci. univ. Jassy, I* **29**, 17 (1943); *Chem. Abstr.*, **42**, 3743 (1948).

Action of Grignard Reagents on Triphenylacetyl Chloride

JANICE L. GREENE,[1] DONALD ABRAHAM, AND HARRY D. ZOOK

Received August 18, 1958

In an attempt to prepare methyl trityl ketone by the addition of methylmagnesium iodide to triphenylacetyl chloride a 67% yield of *ethyl* triphenylacetate was obtained. The ester was identified by analysis and a comparison of the infrared spectrum with that of a sample synthesized from the acyl halide and ethanol. The probable route for the formation of this product is by cleavage of the solvent, ethyl ether, by the acyl chloride in the presence of magnesium iodide or other Lewis–acid component of the Grignard reagent. Cleavage of ether as a minor side reaction in the Grignard process has been reported previously. Small amounts of ethyl *t*-butylacetate were isolated when *t*-butylacetyl chloride was treated with several Grignard reagents.[2] Furthermore, anhydrous magnesium chloride was shown to catalyze the cleavage of ethyl ether by acetyl chloride.[3]



$$Ph_3CCOX \xrightarrow{MX_2} Ph_3C\overset{+}{C}O\ MX_3^- \xrightarrow{Et_2O}$$

$$Ph_3C\overset{O}{\overset{\|}{C}}:\underset{Et}{\overset{+}{\ddot{O}}}:Et\ MX_3^- \longrightarrow Ph_3CCO_2Et + EtX + MX_2$$

The lack of addition by the simplest Grignard reagent and the large amount of ether cleavage by triphenylacetyl chloride was not consistent with the reported preparation of ethyl trityl ketone from this acyl halide and ethylmagnesium iodide.[4] Consequently, this earlier preparation was repeated exactly as described except that the entire product was extracted into carbon tetrachloride for infrared analysis. No carbonyl compounds were present. Instead, the spectrum showed a strong, sharp peak at 2.83 μ characteristic of the hydroxyl group. The product melting at 103–105°, previously called triphenylmethyl ethyl ketone,[4] was identified as 2,2,2-triphenylethanol, identical to that synthesized from sodium triphenylmethide and formaldehyde. This product is formed by the well known reducing action of Grignard reagents containing β-hydrogen atoms.

$$Ph_3CCOCl + C_2H_5MgBr \longrightarrow Ph_3CCHO + C_2H_4 + MgBrCl$$

$$PH_3CCHO + C_2H_5MgBr \longrightarrow Ph_3CCH_2OMgBr + C_2H_4$$

When ethylmagnesium bromide is added to the aliphatic analog, trimethylacetyl chloride, the products are trimethylacetaldehyde (2%), ethyl *t*-butyl ketone (5.5%), neopentyl alcohol (15%) and ethyl-*t*-butylcarbinol (56%). However, in this case, the alcohols are isolated as their trimethylacetates.[5] Both this fact and the formation of ketone illustrate the greater reactivity of the carbonyl group in trimethylacetyl chloride than that in the aromatic acyl halide. Steric hindrance is probably responsible for this difference, for polar factors should increase the electrophilicity of the carbonyl group in triphenylacetyl chloride. To date, no alkyl trityl ketones have been made by the Grignard reaction; in fact, methyl trityl ketone, prepared by the dehydration and rearrangement of 1,1,2-triphenyl-1,2-propanediol,[6] is the only known member of this series.

EXPERIMENTAL

Triphenylacetic acid. A saturated solution of chlorotriphenylmethane, 118 g., 0.425 mole, in 800 ml. of dry ether was added slowly with stirring to an ice cold mixture of 30 g., 1.25 moles, of powdered magnesium, iodine catalyst, and 900 ml. of anhydrous ether. Reaction began immediately. Gentle reflux was maintained during the addition and for 4.5 hr. thereafter. A white solid precipitated during this time. Carbon dioxide gas was bubbled into the mixture until the precipitate dissolved. Hydrolysis by cold dilute hydrochloric acid gave 120 g. (98.5%) of triphenylacetic acid, m.p. 264–265° with decomposition. Recrystallization from 95% ethanol gave material melting at 269–270° without decomposition. The highest m.p. recorded for this compound is 271°.[7] The formation of triphenylmethylmagnesium chloride is highly exothermic. A violent reaction resulting in loss of material occurred when the halide was added in one portion.[8]

Triphenylacetyl chloride. Triphenylacetic acid, 6.4 g., 0.022 mole, was refluxed for 4.5 hr. with 25 ml. of purified thionyl chloride.[9] When cool, the mixture was poured into 75 ml. of 95% ethanol. Much gas was evolved, and white crystalline triphenylacetyl chloride was precipitated; m.p. 127–128° with no decomposition up to 134°. Although the yield was only 2.0 g. (34%), the product was much better than that obtained when the reaction mixture was poured onto ice and the resulting solid recrystallized twice from chloroform. This material melted at 126–127° with evolution of gas. The best m.p. recorded for this compound is 128–129° with decomposition.[10]

In two other preparations, the hot solution was poured into four times its volume of glacial acetic acid. After vigorous evolution of gases, the product crystallized slowly at 0°. Yields of 52 and 54% were obtained with melting points at 127–128° and 125–127°, the latter with evolution of gas.

Reaction of triphenylacetyl chloride and methyl Grignard reagent. To the Grignard solution prepared from 2.3 g., 0.096 mole, of magnesium, 16.0 g., 0.11 mole, of methyl iodide and 100 ml. of dry ether was added 1.7 g., 0.006 mole, of triphenylacetyl chloride. The solution was refluxed for 19

---

(1) Taken in part from the Ph.D. thesis of Janice L. Greene, The Pennsylvania State University, 1958. Present address, Department of Chemistry, The Woman's College of the University of North Carolina, Greensboro, N. C.

(2) F. C. Whitmore, J. S. Whitaker, K. F. Mattil, and A. H. Popkin, *J. Am. Chem. Soc.*, **60**, 2790 (1938).

(3) F. C. Whitmore and W. R. Wheeler, *J. Am. Chem. Soc.*, **60**, 2899 (1938).

(4) J. Schmidlin, *Ber.*, **43**, 1141 (1910); M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice Hall, Inc., Englewood Cliffs, N. J., 1954, p. 763.

(5) R. E. Meyer, Ph.D. thesis, The Pennsylvania State University, 1941.

(6) J. L. Greene and H. D. Zook, *J. Am. Chem. Soc.*, **80**, 3629 (1958); A. McKenzie and J. R. Myles, *Ber.*, **65**, 209 (1932).

(7) P. G. Scholefield, S. T. Bowden and W. J. Jones, *J. Chem. Soc. Ind.*, **66**, 447 (1947).

(8) H. Gilman and E. A. Zoellner, *J. Am. Chem. Soc.*, **51**, 3493 (1929); D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 294.

(9) L. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Co., Boston, Mass., 1955, p. 345.

(10) J. Schmidlin and H. H. Hodgson, *Ber.*, 41, 438 (1908).

hr. and poured with stirring into a 1:1 mixture of ice and concentrated hydrochloric acid. An ethereal solution of the product was washed with water and dried over calcium sulfate to give 1.26 g. (67%) of white solid, m.p. 110–115°. The solid was dissolved in cyclohexane and chromatographed on a 1 × 20 cm. column of Mallinckrodt analytical grade activated silica gel. Development and elution with cyclohexane gave 0.76 g., m.p. 115.8–116.4° from cyclohexane; 116.8–117.8° from methanol. The infrared spectrum in carbon tetrachloride and in a potassium bromide pellet exhibited a carbonyl peak at 5.77 μ. These constants did not correspond to those of methyl trityl ketone, m.p. 138°, C=O absorption maximum at 5.84 μ. Ethyl triphenylacetate has been reported to melt at 116–117°[11] and at 120–121°.[10] The above product was recovered unchanged after 13 hr. reflux with 10% sodium hydroxide solution; however, esters of triphenylacetic acid saponify with difficulty.[10]

Ethyl triphenylacetate was prepared by heating for one hour 2.56 g. of triphenylacetic acid in 15 ml. of purified[9] thionyl chloride, then refluxing the acyl halide for 21.5 hr. with 5 ml. of absolute ethanol. The product was treated with hot alcoholic potassium hydroxide to remove any excess acyl halide, and poured into water. The solid ester, obtained by extraction into ether and crystallization from 95% ethanol, melted at 115–116.5°. A carbon tetrachloride solution of the ester was chromatographed on a 1 × 20 cm. column of silica gel to give a product melting at 116–117° after recrystallization from methanol. The infrared spectrum of this material was identical with that from the reaction of triphenylacetyl chloride and methylmagnesium iodide in ethyl ether.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.54; H, 6.33. Found: C, 83.86; H, 6.40.

Reduction of triphenylacetyl chloride by ethylmagnesium iodide. To 5.0 g., 0.017 mole, of acyl halide in 50 ml. of dry ether was added slowly 60 ml. of 1.4 M ethylmagnesium iodide. Heat and gas were evolved. The gas was collected in a trap cooled by liquid nitrogen and was later expanded at 25° into a 1160-ml. storage system. The final pressure in the system was 424 mm. The infrared spectrum was identical to that of pure ethylene except for a small peak at 8.8 μ which was probably due to ether vapor. Comparison of the absorbancy at 10.98 μ with that of a sample of Matheson C.P. ethylene showed that the gas was 96.5% ethylene. The amount corresponds to 0.026 mole or 76% based on the reduction of the acyl halide through the aldehyde to the primary carbinol.

The residue was hydrolyzed by the addition of 35 ml. of water and 25 ml. of hydrochloric acid. The water layer was extracted with four 20-ml. portions of carbon tetrachloride and concentrated by fractionation through a 12-plate column. The residue from the distillation was made up to 50.0 ml. with carbon tetrachloride. The infrared spectrum contained a strong, sharp OH peak at 2.83 μ and no absorption in the carbonyl region. The solution was washed with sodium thiosulfate, concentrated to 15 ml., diluted hot with an equal volume of ethanol and cooled to 0°. Crystals weighing 1.8 g. were isolated and recrystallized six times from hexane to give 2,2,2-triphenylethanol, m.p. 103–105°.[12]

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.59; H, 6.57. Found: C, 87.29; H, 6.41.

A sample of the carbinol was converted to the acetate, m.p. 135–137°; reported m.p. 136°.[13] The absorbance of the carbinol at 9.43 μ obeyed Beer's law and was used to estimate the total yield of carbinol in the original carbon tetrachloride extract. This amount, 1.3 g., represents a yield of 30% of the primary alcohol. The OH peak at 2.83 μ, however, was larger than that calculated from this amount of carbinol and indicates the presence of another more soluble alcohol in the mother liquors. One possibility is ethyltritylcarbinol from the addition of ethylmagnesium iodide to the intermediate triphenylacetaldehyde.

COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PA.

---

[11] J. F. Norris and A. Cresswell, *J. Am. Chem. Soc.*, **56**, 423 (1934).

[12] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1119 (1952).

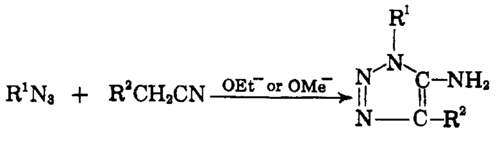
[13] J. Danilow, *J. Russ. Phys. Chem. Soc.*, **51**, 122 (1919).

Improved Procedure for Condensation of Alkyl Azides with Phenylacetonitrile to Form *vic*-Triazoles

EUGENE LIEBER,[1] C. N. R. RAO, AND T. V. RAJKUMAR

Received August 18, 1958

The elegant method for the synthesis of 1,4-disubstituted-5-amino-1,2,3-triazoles, III, first described by Dimroth,[2] involving the reaction of an organic azide, I, with an acetonitrile, II, in the presence of stoichiometric quantities of sodium ethoxide gives excellent yields for those cases in which the R substituent of I is an aromatic ring.[3] The yields were found to be poor when the benzyl and alkyl azides were employed. In the case of benzyl azide long periods of heating were required to effect condensation; even greater difficulties were experienced for alkyl azides in which R^1 was C_2H_5 and n-C_6H_{13}. Only in the case of ethyl azide was it possible to obtain a small quantity of the expected triazole; the major product when R^1 was C_2H_5 and n-C_6H_{13} consisted of an unknown substances[3a] whose elemental composition corresponded to the addition of two moles of II (R^2 = C_6H_5) and one mole of I (R^1 = C_2H_5 and n-C_6H_{13}). This communication reports on a significant improvement in the synthesis of III (R^1 = $C_6H_5CH_2$) and a new triazole, R^1 = n-C_6H_{13}, hitherto unattainable by the previous procedures.[3]



I II III ($R^2 = C_6H_5$)

When n-hexyl azide was stirred at room temperature with II (R^2 = C_6H_5) in anhydrous tetrahydrofuran (THF) as solvent in the presence of an equimolar amount of potassium *tert*-butoxide (KTB), a practically quantitative yield of III (R^1 = n-C_6H_{13}) was obtained. Previous experiments[3a] using benzyl azide gave a 59% yield of a very impure and difficultly purifiable III (R^1 = $C_6H_5CH_2$)

---

[1] To whom all correspondence should be addressed.

[2] O. Dimroth, *Ber.*, **35**, 1034 (1902).

[3] (a) E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, **22**, 654 (1957); (b) E. Lieber, T. S. Chao, and C. N. R. Rao, *Org. Syntheses*, **37**, 26 (1957).