[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY, AND AIN SHAMS UNIVERSITY, CAIRO]

Photochemical Reactions in Sunlight. Part XIX. Experiments with Desoxybenzoin Derivatives

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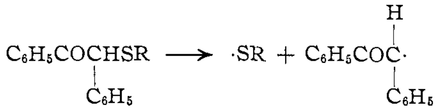
Benzoyldiphenylmethane in benzene solution on illumination by sunlight forms 1,1,2,2-tetraphenylethane and benzaldehyde. The desoxybenzoin derivatives (IIa-e) under these conditions yielded didesyl; the mechanism of the reactions is discussed.

Benzoyldiphenylmethane (I) in benzene solutions and an atmosphere of nitrogen or carbon dioxide, on exposure to sunlight, has been found to give, *inter alia*, 1,1,2,2-tetraphenylethane and benzaldehyde.

$$\underset{\text{I}}{2C_6H_5COCH(C_6H_5)_2} \xrightarrow{\text{light}} (C_6H_5)_2CHCH(C_6H_5)_2 + C_6H_5CHO$$

The mechanism may involve the decomposition of I to benzoyl and diphenylmethyl radicals, dimerization of the diphenylmethyl radical to tetraphenylethane and abstraction of a hydrogen atom from I by the benzoyl radical to form benzaldehyde. Another possible route is attack of the diphenylmethyl radical on I to give tetraphenylethane and a benzoyl radical.

The action of sunlight on desoxybenzoin derivatives (IIa-e) also has been investigated. Didesyl crystals of high purity separated during the exposure in every case. In some, *e.g.*, IIb, the much more soluble stereoisomer, isodidesyl, was obtained.



$$\underset{\text{II}}{C_6H_5CO\underset{C_6H_5}{CH}SR} \longrightarrow \cdot SR + \underset{\text{III}}{C_6H_5CO\overset{H}{\underset{C_6H_5}{C}}\cdot} \quad \text{eq. 1}$$

IIa, R = C_6H_5 d, R = $C_6H_4CH_3(p)$

b, R = $C_6H_4CH_3(o)$ e, R = $SCOC_6H_5$

c, R = $C_6H_4CH_3(m)$

$$\text{III} + \text{II} \longrightarrow (C_6H_5CO\underset{\cdot}{C}HC_6H_5)_2 + \cdot SR \quad \text{eq. 2}$$

In the reactions of IIa and the new tolyl derivatives IIb-d it is probable that ·SR forms (eq. 1), and goes to thiophenol (smell and color reaction). However, neither thiophenol nor one of its derivatives could be separated. The dibenzoyl sulfide obtained from the reaction of desyl thiobenzoate (IIe) may be presumed to result from dimerization of the free monovalent sulfur (thiyl) radical.

The sulfur compounds may photodissociate to form the free desyl radical III which dimerizes. The didesyl might also be formed by the action of the desyl radical on II (eq. 2).

The new tolyl derivatives IIb–d were prepared by the action of the respective thiocresols on desyl chloride, $C_6H_5COCH(Cl)C_6H_5$, in the presence of alcoholic sodium ethoxide; this method was also successful in the preparation of IIa.

Acknowledgment.—We wish to thank M. Nosseir for repeating some of the experiments.

Experimental

The benzene used in the photoexperiments was free from toluene[1] and thiophene and had been dried over sodium. The reaction mixtures were placed in Schlenk tubes[2] of Pyrex glass, the air displaced by dry carbon dioxide or nitrogen and the tube sealed. Control experiments in the dark showed no reaction.

Photochemical Reaction of Benzoyldiphenylmethane.—Benzoyldiphenylmethane[3] (0.4 g.) in 10 ml. of benzene was exposed to sunlight for two weeks (May); the solution turned yellow during this period. On concentration to 2 ml., cooling and filtration, 0.08 g. of crystals was obtained which showed, without further purification, m.p. 209° and no depression on admixture with an authentic sample of symmetrical tetraphenylethane.[4] The filtrate from above, upon further concentration at room temperature, yielded a residue which consisted of crystals, oils and resins and had a very strong smell of benzaldehyde. The residue was dissolved in alcohol, treated with 2,4-dinitrophenylhydrazine and yielded the 2,4-dinitrophenylhydrazone of benzaldehyde (m.p. and mixed m.p.).

Anal. Calcd. for $C_{26}H_{22}$: C, 93.4; H, 6.6. Found: C, 93.0; H, 7.0.

Similar reactions in the presence of 0.5 g. of freshly prepared anhydrous sodium sulfate and 0.5 g. of anhydrous sodium carbonate gave results as above, indicating that there was no influence on the photoreaction of traces of moisture or hydrochloric acid (from carbon dioxide generated from marble and hydrochloric acid).

Photochemical Reactions of (IIa–d).—The procedures for IIa–d were very similar; the following is given as an example.

A solution of 2 g. of *o*-cresyl desyl sulfide IIb in 15 ml. of benzene and a CO_2 atmosphere was exposed to sunlight for one month (January). The colorless crystals (0.2 g.) which separated were filtered, crystallized from benzene and found to be didesyl (m.p., mixed[5] m.p. 255° and analysis). Concentration of the filtrate gave colorless needles which were recrystallized from petroleum ether (b.p. 80–100°) and found to be isodidesyl (m.p., mixed m.p. and analysis).

Glacial acetic acid and some small crystals of sodium nitrite added to the filtrate before concentration gave a red color, indicating the presence of *o*-thiocresol.[6]

These compounds IIa–d were refluxed in benzene for six hours and recovered unchanged.

Photochemical Reaction of Desyl Thiobenzoate (IIe).—One gram of IIe[7] in 15 ml. of benzene in a nitrogen atmosphere was exposed to sunlight for 16 days (May). The tube was allowed to stand for some hours at 30° and the crystals (0.105 g.) filtered from the orange-yellow solution. Crystallization from benzene gave didesyl (m.p. and mixed m.p.).[5]

Concentration of the filtrate yielded another crop of didesyl. On further concentration crystals were obtained which after crystallization from petroleum ether (b.p. 50–60°) were proved to be dibenzoyl disulfide (m.p., mixed m.p. and analysis).

When IIe was refluxed for 6 hours in benzene, it was recovered unchanged.

***p*-Cresyl Desyl Sulfide (IId).**—One gram of *p*-thiocresol in alcoholic sodium ethoxide (0.2 g. of sodium in 10 ml. of

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(1) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 997 (1947).

(2) W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913); Houben, "Die Methoden der organischen Chemie," 2nd edn., Vol. IV, p. 960.

(3) Delacre, *Bull. soc. chim.*, [3] **13**, 859 (1895).

(4) A. Zagoumenny, *Ann.*, **184**, 176 (1877), and J. F. Norris, R. Thomas and B. M. Brown, *Ber.*, **43**, 2959 (1910).

(5) E. Knoevenagel, *Ber.*, **21**, 1358 (1888).

(6) H. Rheinboldt, *ibid.*, **60**, 184 (1927).

(7) A. Schönberg and Y. Iskander, *J. Chem. Soc.*, 90 (1942).

absolute alcohol) and 2 g. of desyl chloride[8] were heated on a water-bath for about five minutes. After cooling 20 ml. of water was added and the mixture cooled in an ice-bath. The crystals which formed (2 g.) were recrystallized first from alcohol and then from petroleum ether (b.p. 50–60°), giving colorless needles m.p. 79°.

Anal. Calcd. for $C_{21}H_{18}OS$: C, 79.3; H, 5.6; S, 10.1. Found: C, 79.0; H, 5.7; S, 10.0.

o-**Cresyl Desyl Sulfide** (IIb).—This was prepared as in the case of IId; colorless crystals, m.p. 115°, were obtained from petroleum ether (b.p. 50–60°).

Anal. Calcd. for $C_{21}H_{18}OS$: C, 79.3; H, 5.6; S, 10.1. Found: C, 78.7; H, 5.7; S, 10.2.

Phenyl Desyl Sulfide[9] (IIa).—This was prepared like IId, m.p. 83–84°.

m-**Cresyl Desyl Sulfide** (IIc).—A solution of 1.9 g. of *m*-thiocresol in alcoholic sodium ethoxide (0.3 g. of sodium in 15 ml. of absolute alcohol) was treated with 3.5 g. of desyl chloride and heated on a water-bath for 10 minutes. Water (20 ml.) was added, the solution extracted with ether, the extract dried over anhydrous sodium sulfate and the ether removed. The oil obtained was washed several times with petroleum ether (b.p. 50–60°) and cooled. The colorless solid which separated was crystallized from alcohol (1.99 g., m.p. 63°).

Anal. Calcd. for $C_{21}H_{18}OS$: C, 79.3; H, 5.6; S, 10.1. Found: C, 79.6; H, 5.9; S, 10.0.

m-Cresyl desyl sulfide is insoluble in 5% aqueous sodium hydroxide solution and gives no color reaction in acetic acid with sodium nitrite.[6] When treated with concentrated sulfuric acid, a yellow-brown coloration was obtained, which turned violet in a few minutes.

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[8] A. M. Ward, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 159.

[9] W. A. Mitchel and S. Smiles, *J. Chem. Soc.*, 1529 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Action of Aluminum Chloride on Alkylbenzenes. V

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When 1,3-dimethyl-4-*n*-propylbenzene is warmed with aluminum chloride, the propyl group migrates to the 5-position without extensive isomerization. Under the same conditions, 1,3-dimethyl-4-isopropylbenzene yields 1,3-dimethyl-5-isopropylbenzene. The alkylation of *m*-xylene with *n*-propyl chloride yields 1,3-dimethyl-5-*n*-propylbenzene, 1,3-dimethyl-5-isopropylbenzene and a small amount of 1,3,4-trialkylbenzene.

Recent work from this Laboratory[2] has shown that when 1,3-dimethyl-4-*n*-butylbenzene was warmed with aluminum chloride, the *n*-butyl group migrated to the 5-position without extensive isomerization. This fact led us to repeat our earlier experiments with 1,3-dimethyl-4-*n*-propylbenzene.[3]

It has now been established by both chemical and spectroscopic evidence that the principal changes which take place when these trialkylbenzenes are warmed on a steam-bath with aluminum chloride are

1,3-dimethyl-4-*n*-propylbenzene ⟶
I
1,3-dimethyl-5-*n*-propylbenzene
II
1,3-dimethyl-4-isopropylbenzene ⟶
III
1,3-dimethyl-5-isopropylbenzene
IV
1,2,4-tri-*n*-propylbenzene ⟶ 1,3,5-tri-*n*-propylbenzene
V VI

The migrating *n*-propyl group was not extensively isomerized as previously reported.

The identity of the rearrangement products II and IV was established by comparison of their infrared spectra with the spectra of authentic II[4] and with IV prepared by the alkylation of *m*-xylene with isopropyl chloride. Mixture melting points of the trinitro derivatives furnished the chemical evidence for the identity of the hydrocarbons. The spectrum of IV was nearly identical with that of IV from *m*-xylene and isopropyl chloride. Products II and IV contained 28 and 13%, respectively, of 1,3,4-trialkylbenzene.

Neither the spectrum of II nor the melting point data from the trinitro derivatives exclude the possible presence of some IV in the rearrangement product from I. The resolving power of our infrared spectrophotometer is not now sufficiently good to detect and determine IV in this product. Roberts and Brandenberger[5] have used isotopic tracer methods to demonstrate that the aluminum chloride catalyzed disproportionation of *n*-(β^{14}-C)-propylbenzene results in a partial isomerization of the *n*-propyl group. A known mixture which we prepared containing 15% of IV and 85% of II yielded the trinitro derivative of II which melted at 98.5–99.5° after two recrystallizations and was constant at 99.5–100° after the third recrystallization. Similar results were obtained from the nitration of a mixture containing 10% of 1,3-dimethyl-5-*sec*-butylbenzene and 90% of 1,3-dimethyl-5-*n*-butylbenzene. It is entirely possible that our product from the action of aluminum chloride on 1,3-dimethyl-4-*n*-butylbenzene[2] contained some 1,3-dimethyl-5-*sec*-butylbenzene.

The alkylation of *m*-xylene with *n*-propyl chloride yielded a mixture of II and IV in a ratio of about 1.8:1 based on the weights of the 1,3,5-trialkylbenzene fractions. They were identified by means of their trinitro derivatives.

The alkylation of *m*-xylene with isopropyl alcohol

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[1] Abstracted from the dissertation submitted by J. M. Shackelford for the degree of Doctor of Philosophy, August, 1955.

[2] D. V. Nightingale and J. M. Shackelford, THIS JOURNAL, **76**, 5767 (1954).

[3] D. V. Nightingale and B. Carton, *ibid.*, **62**, 280 (1940).

[4] The authentic 1,3-dimethyl-5-*n*-propylbenzene, 99.3% pure, was kindly furnished to us by Dr. K. W. Greenlee of the American Petroleum Institute Research Project 45 (APIRP45), C. E. Boord, Director, a project of the Ohio State University Research Foundation; *J. Org. Chem.*, **19**, 923 (1945).

[5] R. M. Roberts and S. G. Brandenberger, *Chemistry and Industry*, 227 (1955).