Rendiconti Accademia Nazionale delle Scienze detta dei XL
Memorie di Scienze Fisiche e Naturali
ISBN 987-88-548-5146-7
DOI 10.4399/978885485146714
pag. 175–185

The development of photochemistry in Italy after the First World War

Maurizio D'Auria

1. Summary

The work of coworker of Paternò, Remo de Fazi, will be examined showing his important contribution to the development of the photochemical studies in Italy after the First World War. The aim of this study is the demonstration that the First World War signed a stop in the research in photochemistry in Italy, but this experience was not completely destroyed and some relevant studies continued after the War.

2. Riassunto

Verrà esaminato il lavoro di un collaboratore di Paternò, Remo de Fazi, mostrando il suo importante contributo allo sviluppo degli studi in fotochimica in Italia dopo la prima Guerra Mondiale. La finalità di questo studio è quella di dimostrare che la prima Guerra Mondiale segnò certamente una fermata nella ricerca in fotochimica in Italia, ma questa esperienza non fu completamente distrutta ed alcuni studi significativi continuarono anche dopo la guerra.

3. The development of photochemistry in Italy

Most of the recent works on the history of photochemistry assign a crucial role in the development of this research field to the Italian scientist Giacomo Ciamician [2,3]. Only recently, some authors noted that the cultural environment in Italy in that period could produce

some important contributions, not only by Ciamician, but also by Paternò [1]. In this case, the definition of "belle époque" of photochemistry has been used, also considering that the cultural production in photochemistry by Italian researchers finished with the First World War.

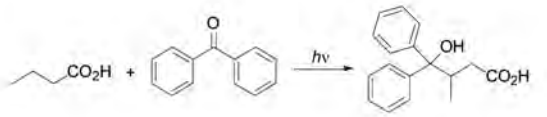
In this article we want to note that, in the Italian cultural environment at the beginning of the xx century, there are several actors participating to the efforts in the development of the use of light in chemistry, and that the research in photochemistry does not finish at the beginning of the war, but continued considering the scientific work of some pupils of Paternò.

The photochemistry in Italy was born as organic photochemistry. The first articles of Ciamician on photochemistry were on the reduction of quinone to hydroquinone and the reduction of nitrobenzene [15–17]. Few years later, Maria Bakunin reported the photochemical *E,Z* isomerization of 2–phenyl–*p*–nitrocinnamic acid [5,35,54]. In 1902 Ciamician published his results on the photodimerization in solid phase of cinnamic acid, stilbene, and cumarin [21,22]. In the period between 1902 and 1916, Bakunin studied the dimerization reaction of 2–phenyl–4–nitroindone [6–10]. In 1908 Ciamician reported the [2+2] intramolecular cycloaddition of carvone [28]. Between 1900 and 1908 Ciamician described the reaction of photoreduction of the ketones in the presence of alcohols [18, 19, 31, 32]. In the period 1901–1906 Ciamician described the reduction reactions of aromatic nitrocompounds in the presence of alcohols and aldehydes [20, 23–25]. Between 1907 and 1909 Ciamician reported the first examples of Norrish Type I reactions [26–29]. In the period between 1908 and 1914 all the articles published by Paternò on the photochemistry appeared [55, 56, 58–66]. In 1909 he described the reaction of carbonyl compounds with alkenes to give the corresponding oxetanes [36, 58]. In the period 1910–1914 both Ciamician and Paternò described the reactions of ketones with compounds bearing benzylic hydrogens [30, 33, 34, 59–65].

After this period Ciamician did not publish an article on photochemistry. No one of his assistants worked in photochemistry. Paternò also did not work in photochemistry. The idea that after the First World War the study in photochemistry in Italy died was born from these consideration. However, Paternò in 1915 published a work not considered by his bibliography [67]. He reports part of the results

obtained in the photochemical reaction of butyric acid with benzophenone [57]. In Note V of the series "Synthesis in organic chemistry by means of light" he described that acetic acid, irradiated in the presence of benzophenone, did not react, while phenylacetic acid gave triphenyllactic acid [60]. In this field Paternò describes part of the results obtained irradiating butyric acid in the presence of benzophenone. He notes both that at the opening of the tube a significant evolution of carbon dioxide was observed and one of the reaction products was propyl butyrate. Furthermore, he asserted that the accurate study of all the reaction products would be performed by his coworker dr. Remo de Fazi. Remo de Fazi has been a coauthor of the Note X of the series "Synthesis in organic chemistry by means of light" [61].

Remo de Fazi was born in Montefiascone at 1891 and obtained the degree in chemistry at 1914. At 1928 he was full professor in pharmaceutical chemistry at the University of Messina. The, three years later, he obtained the chair at the University of Pisa, where he remained until 1961. He died in 1979. De Fazi performed the task assigned him by Paternò and describes all the products isolated in the reaction between butyric acid and benzophenone [37]. In this article de Fazi isolated and identified, beyond propyl butyrate, the main product of the reaction (Scheme 1). The product resulted from the same type of the observed reactivity in phenylacetic acid: in this case, the stabilized benzylic radical could not be formed and the reaction occurred at the adjacent carbon.



Scheme 1. The reaction of butyric acid with benzophenone

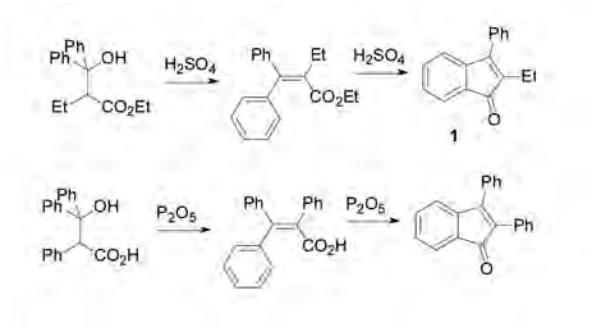
Some years later de Fazi ri–examined the reaction of phenylacetic acid with benzophenone showing that, also in this case, little amounts of benzyl phenylacetate can be obtained [45].

De Fazi had centered his studied von the esters of phenyllactic acids, of the same type of those obtained by Paternò. In some articles of 1915 he observed that ethyl α–ethyl–β,β–diphenyllactate could be obtained

through a reaction between ethyl 2–bromobutyrate and benzophenone in the presence of zinc [49, 50]. This product in the presence of sulfuric acid gave the corresponding 2–ethyl–3–phenylindone (Scheme 2).

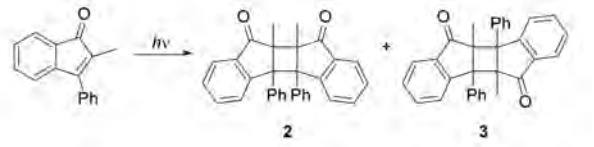
The same reaction, in this case performed with phosphoric anhydride, was obtained by de Fazi on the product obtained by Paternò in the photochemical reaction between phenylacetic acid and benzophenone (Scheme 2) [39, 50].

In a work published on 1921, de Fazi showed that Z–α–methylcinnamic acid gave the corresponding indone if treated with sulfuric acid, while the *E*–isomer, obtained through UV irradiation, did not be converted into the indone [41].



Scheme 2. Synthesis of the indones

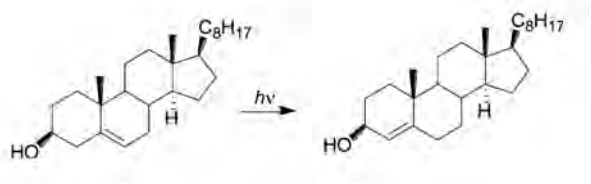
After these preliminary studies, starting from a photochemical reaction found by Paternò, de Fazi started to study the photochemical behavior of these indone. He found, in some preliminary notes, that α–methyl–β–phenylindone, irradiated with an UV lamp, gave two dimers; however, he did not was able to discriminate between these two structures (Scheme 3) [42, 43].



Scheme 3. Photochemical behaviour of the indones

The complete work in this field appeared in the same year. The reaction gave two dimers in different yields (56 and 8%). The main product was 2 while 3 was the by–product [44]. When the reaction was performed under solar irradiation the main product 1 was obtained in higher yields in the presence of traces of another dimer. On the contrary, the compound 1 did not give dimers [46]. Furthermore, he found that the dimers are not photochemically stable. He found that the dimers obtained by sulfuric acid treatment of the indones (two compounds), after irradiation, can be converted in other two dimer derivatives. On the contrary, irradiation of the dimers obtained through photochemical irradiation of α–methyl–β–phenylindone, gave a retrocycloaddition reaction reforming the indone [46, 52].

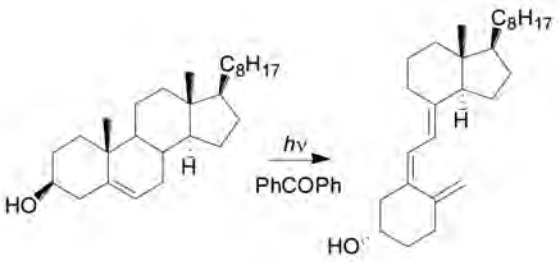
Connected with the work on the indones de Fazi started to study the structure of cholesterol, showing that the irradiation of cholesterol under solar light induced the formation of an isomeric product (Scheme 4) [49]. de Fazi could not give the structure of the product, but the reaction has been studied several years later [53].



Scheme 4. Photochemical isomerization of cholesterol

In an another communication, coauthor Augusto Banchetti, reported the formation of a dimer in the reaction of cholesterol in the presence of benzophenone, together with dihydrocholesterol [50]. The reaction between cholesterol and benzophenone is now theobject of an intensive study [4]. Banchetti continued the study on the photochemistry of ketones. First, he studied the oxidation of some alcohols (related to cholesterol, such *trans*–β–decalol) in the presence of benzophenone [11], then the formation of tetraphenylethene oxide in the reaction between benzophenone in isopropyl alcohol in the presence of hydrogen chloride [12]. Finally, he confirmed the formation of 1, 1, 2, 2–tetraphenylethanol in the reaction between

diphenylmethane and benzophenone [13]. The most important contribution of Banchetti to the photochemistry was the identificatione of Vitamin D3 in the reaction of cholesterol and acetylcholesterol in the presence of benzophenone (Scheme 5) [14].



Scheme 5. Photochemistry of cholesterol in the presence of benzophenone

de Fazi studied also the reaction between acenaphthene and benzaldehyde under solar irradiation. He found that the main products were the polymers of benzaldehyde but he found also the presence of a coupling product, a ketone, deriving from a Paternò–Büchi reaction between acenaphthylene (obtained through reaction between acenaphthene and benzaldehyde) and benzaldehyde, followed by oxetane cleavage [48].

Furthermore, he found the sterilizing properties of UV irradiation showing that alcoholic fermentation by *Saccaromyces Cerevisiae* of previously irradiated aqueous solutions of glucose worked better that on control non irradiated solutions [47].

In the last photochemical note de Fazi defended the results of Paternò in the synthesis of triphenyllactic acid against the work of D. Ivanoff and T. Ivanoff on Comptes Rendus where the authors questioned the identification the product [51].

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Maurizio D'Auria
Dipartimento di Chimica A. M. Tamburro
Università degli Studi della Basilicata
maurizio.dauria@unibas.it