COMMUNICATIONS

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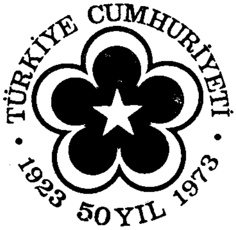
DE L'UNIVERSTÉ D'ANKARA
ANNÉE 1973

Série B: Chimie

CUMHURİYETİN 50. YILI



Faculté Des Sciences de l'Université D'Ankara
Ankara, Turquie

ÖNSÖZ

Cumhuriyetimizin kuruluşunun 50. yıl dönümünde, Ankara Üniversitesi Fen Fakültesinin Dekanı olarak bulunmam benim için çok mutlu bir raslantıdır.

Yarım yüzyıl önce büyük bir azim ile milletini bir bütün halinde toplayan büyük kurtarıcımız Atatürk'ün aziz hatırası önünde memleketimizin bütün bilim adamlarının saygıyla eğildiğine eminim. İnsanlık haysiyet ve özgürlüğüne göz diken, kıskanç ve hırslı ruhların aldatmaya çalıştığı gençlerimiz, ümit ederimki, Atatürk'ün kendilerine emanet ettiği bu Cumhuriyet'in, içine atılmaya çalışıldığı durumu artık anlamışlar ve ancak Atatürk'ün kendilerine gösterdiği "hayatta en hakiki mürşit olan ilim" yolunda çalışarak memleketlerine hizmet edebileceklerinin bilincine varmışlardır.

Gençlerimizin bu teknik ve uzay çağında bir Fen Fakültesi öğrencisi olmanın değerini çok iyi takdir ettiklerine ve fedakâr milletimizin kendilerine sağladığı bu imkânı en iyi şekilde kullanmaya azimli olduklarına inanmaktayım. Fakültemizde son yıllarda % 80'e çıkan başarı durumu da bunun delilidir.

Öğrencilerimizin ve Fakültemiz mensuplarının Türkiyenin geleceğine katkıda bulunmak için daha kuvvetle çalışacaklarına bu yıl dönümünde bir kere daha söz veriyoruz.

DEKAN

Prof. Dr. Sevinç KAROL

TABLE DES MATTIERES

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Structure of Potassium Salt of 2,4-Dinitrophenyl Diethylmalonate

by

NECLÂ GÜNDÜZ and ÇAKIL ERK

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Communications de la Faculté des Sciences de l'Université d'Ankara

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Structure of Potassium Salt of 2,4-Dinitrophenyl Diethylmalonate

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University of Ankara Turkey

ABSTRACT

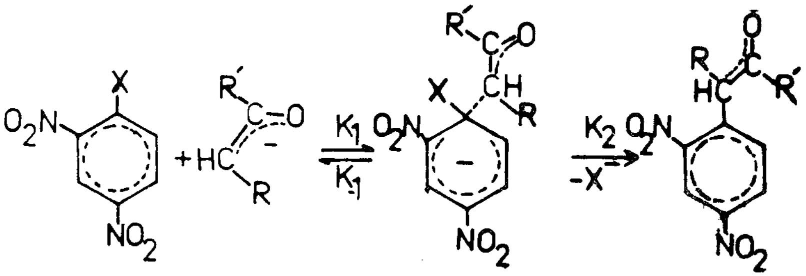
The formation of coloured species from α- dinitro phenylated-β- di carbonyls in basic media was investigated. Evidence besed mainly upon nuclear magnetic resonance IR spectroscopy and elemental analysis suggest that the red coloured solid compounds obtained are alkali derivatives of dinitrophenylated- β- diketo compounds forming by loss of active α- proton.

INTRODUCTION

Despite the investigations of aromatic nucleophilic substutions (1) with great number of nucleophiles, the reactions of carbanions particularly stabilized by carboxy alkyl carbonyl or cyano groups have not been widely investigated although they some time provide the difficulties because of their ambient character (2).

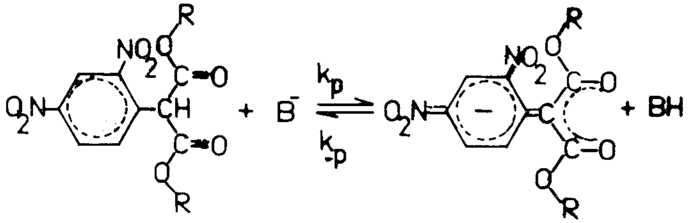
Some authors, however, reported that the common active methylene compounds react with 2,4– dinitro and 2,6– dinitro halogene benzenes at the carbon atom (3).

Moreover, the potential investigations on the janowsky reactions verified that the substitution are generally involved on the carbon atom of the ambident anion (4). Via covalently bonded σ–complex, as illustrated.



No evidence has been obtained for the formation of some compounds involving the enol form of the conjugated base. However, inability to detect a product derived from a particular ketonic conjugate base ion does not, of course, preclude the existence of that ion in the system studied (5). In the earlier study, the reactions of 2,4- dinitro and 2,6- dinitro halolene benzene with the potassium salts of various active methylene compounds were investigated (6). Reaction rates have been determined in DMSO and found to be so fast that they could be determined by spectroscopic methods. We therefore followed the rate of formation of some coloured species. The similar compounds was also reported (7) that they form the 2,4- dinitro-benzylic anion by loss of proton in the presence of either mother carbanion or any base available, as simply described.

(2)



In the present work we tried to investigate the probable structure of the coloured compounds in order to support the earlier suggestions. We therefore isolated and purified the potassium derivative of diethyl (2,4- dinitro phenyl) malonate which gives the same UV visible spectra with the solutions those obtained from potassium diethylmalonate and 2,4 - dinitro halogene benzenes in DMSO.

RESULTS

The pmr spectrum was consistent with the proposed structure (Fig. 1) Showing on ABX pattern in aromatic range and a common A_2 B_2 pattern assigned to ethyl protons (Table 1). IR spectrums both for the diethyl(2,4- dinitro phenyl)malonate and its potassio derivative displayed as Fig. 3 and Fig. 2.

TABLE I (*)

PMR Spectra of diethyl (2,4- dinitrophenyl) malonate in Acetone-d_6

	$\surd H_3$	$\surd H_5$	$\surd H_6$	J_{35}	J_{56}	J_{63}	$\surd CH_2$	$\surd CH_3$	$\surd CH$
2,4- DNPDEMH	9.38	7.70	7.17	2.5	9.4	0	4.26	1.26	5.48
2,4– DNPDEM$^-$K$^+$	8.46	7.96	7.71	2.5	9.5	0	4.93	1.08	

(*) Shfit positions given were walculated according to the first order approach for ABX pattern, and denoted by the delta scale, low fields shifts are shown as positive ppm values relative to TMS.

DISCUSSION

The spectroscopic evidence indicates that the formation of intense colour which appear to be instantaneous not only at room temperature but also at low temperature, is due to a loss of α– proton (Eqn. 2).

The base, because of the higher acidity of dinitro-phenylated enol (8) readily undergoes the abstraction of activated α- proton forming a resonance stabilized dinitro benylic anion.

From the PMR spectra it is quite appearant the signal of the mother compound at 5.48 ppm (rel area = 1) assigned to the C-α-proton, has not appeared at the PMR spectra of anion indicating the loss of it. In fact, with the similar compounds we have also found that the proton transfer rate was quite high as reported by Caldin who worked on the p- nitro benzyl cyanide in basic media (9).

The ring protons of anion appear to be more shilded as compare to the mother compound. It is nevertheless expected that the presence of the negative charge oposes the deshielding effect assoiated with the diamagnetic anistropy of the π- electron system resulting the up field shifts (10). The observed effect is obviously not the same in magnitude on the ring protons, the C-5 proton is most shielded while the C-6 proton is less shielded as to their position on the PMR spectrum of the mother compound. The shielding on the C-6 proton is possibly both influenced from the diamagnetic anisotropy of the carbonyl group which is then likely to be in the plane of the aromatic ring and the negative charge delocalized on the system.

It is also of interest that the IR spectra of potassium derivative of the anion in KBr (Fig. 2) we could not observe any appreciable absorption above 1680 cm $^{-1}$ (Fig. 2) despite the reported spectra for the sodium derivative by Boudet (11) regarding a sharp band at 1727 cm $^{-1}$ and a medium band at 1745 cm $^{-1}$. The mentioned study, however, has already been disproved by Shein and Ivanova (12). The bands observed at the 1680 cm $^{-1}$ and 1660 cm $^{-1}$ could be assigned to the carbonyl stretching of the ester carbonyl, frequency fall is around 75 cm $^{-1}$ presumably because of the increased conjugation resulting from the charge delocalisation by formation of the anion (13). It is somewhat in agreement with the fact that the increased contribution of the resonance form involving the C^{+}-O^{-} structure the band lengthens and carbonyl frequency usually falls (13).

However, in the reported studies of Boudet (11) and of Ivanova (12) this bond has been attributed to that of the cyclohexadiene moiety. This is unlikely just because of the evidence that we could not observe such absorption in the mentioned range of IR spectra of similar compounds, provided that the carbonly group is not available (8).

The bond which also exists in the similar systems at the 1595 cm $^{-1}$ may therefore be assigned to the C=C skeletal in plane vibrations which appear at 1610 cm $^{-1}$ in the spectra of mother compound. The band at the 1555 cm $^{-1}$ may also be assigned to to the same mode although it does not appear in the mother compounds spectra (fig. 3), however, the increased conjugation usually produces very marked enhancement of the band intensity (13) as well as frequency falls. The bands to be assigned to the assymetric strecthings of the-NO_2 at 1530 cm $^{-1}$ are medium in intensity which may be attributed to the steric effects while the band at 1340 cm $^{-1}$ is quite intense a well as broad indicating (from the symetric strechtings) the negative charge delocalized (14). It is therefore concluded that the formation way of potassium derivative of diethyl (2,4– dinitrophenyl) malonate which is not only stable in organic solvent but also in water solution is loss of α-proton and the stability is also, because of the delocalization of the negative charge, on the carbonyl groups as well as on the nitro groups. In such a system the considerable conjugation is therefore quite likely.

Although the aromatic ring and the β- diketo ester groups are not considered to be completely coplanar due to the butressing effect of the o-nitro group, theoretical considerations, however, indicate that the resonnance is not severly inhibited until the interplanar angle becomes quite large (15).

EXPERIMENTAL

Diethyl 2,4- dinitrophenylmalonate was prepared from 2,4- dinitro bromobenzene and potassium derivative of diethyl malonate following the same procedure which was described in the earlier study (6). After acidification, the reaction mixture treated by diisoprophyl ether and the ether solution was treated with 1 N KOH solution, then red precipitate was then filtered and washed first with some water and the with diethyl ether. the red product was recrystallized from tetrahydrofuran, red micro crystals, decomposed at 191 °C. Analytical results Support the data obtained from Pmr spectrum (Found: C; 40, 85, H; 3,44, N; 7.34 calculated C; 41, 16, H; 3.16, N; 7.38 for C_{13} H_{13} O_8 K. H_2O)

Solvent acetone-d_6 (Merck), (% 99.5 D) was used without further purification IR spectra were run on a Perkin-Elmer Model 257 Grating Spectrophotometer. PMR spectra were run on a Varian Associate Model A- 60A spctrometer operating at a frequency of 60 MHz tetramethylsilane was incorporated in the solvents as an internal standard.

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ÖZET

α- dinitro fenil β- di karbonillerin bazik ortamdaki renkli bileşikleri incelendi N. M. R. spektroskopisi ve I. R. Spektroskopisi sonuçları, elde edilen katı renkli kırmızı bileşiklerin dinitro fenilli β-dikarbonilli bileşiklerde bir aktif protoun yerine alkali metalinin, geçmesi ile meydana geldiğini göstermektedir.

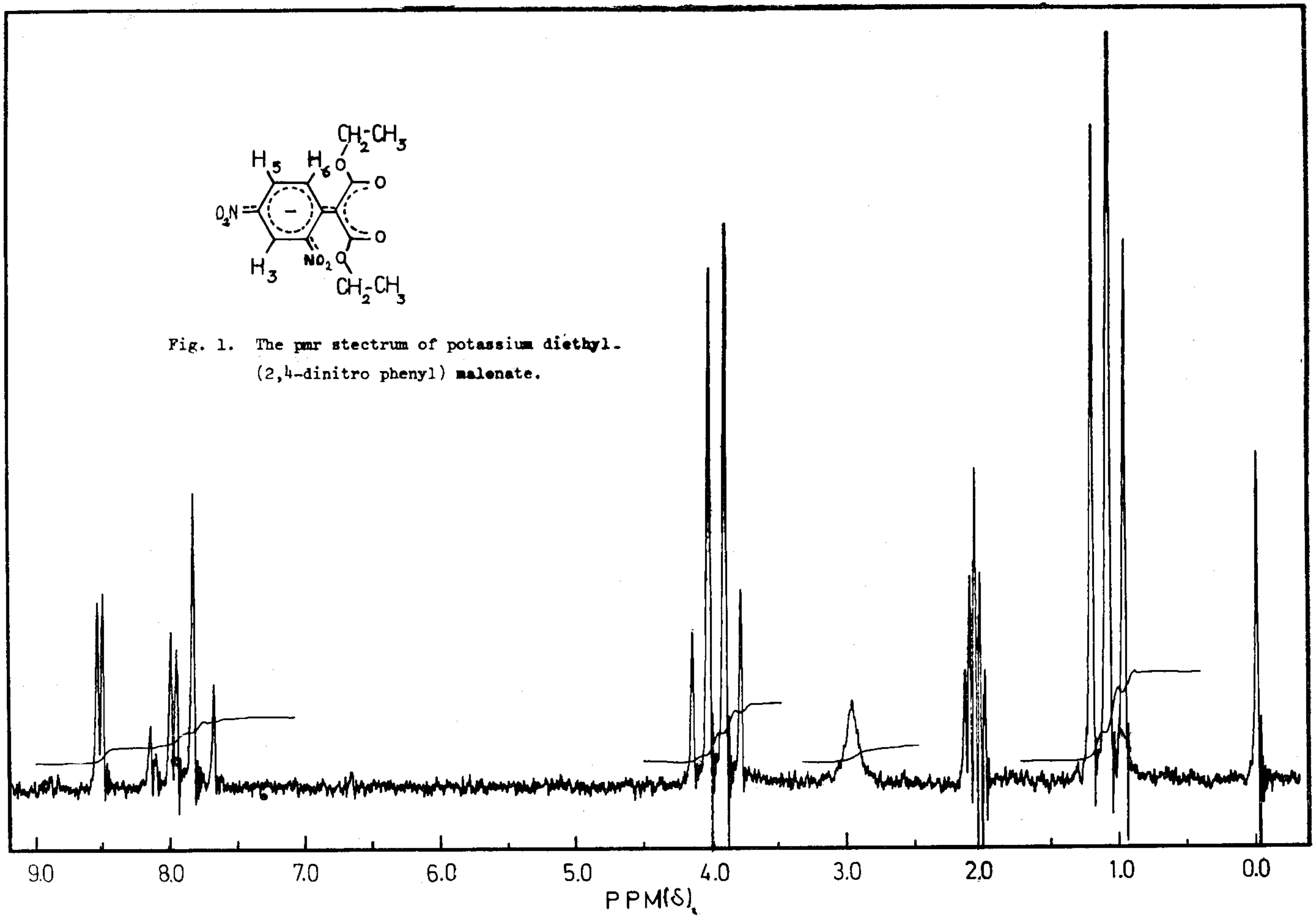

Fig. 1. The pmr stectrum of potassium diethyl-(2,4-dinitro phenyl) malenate.

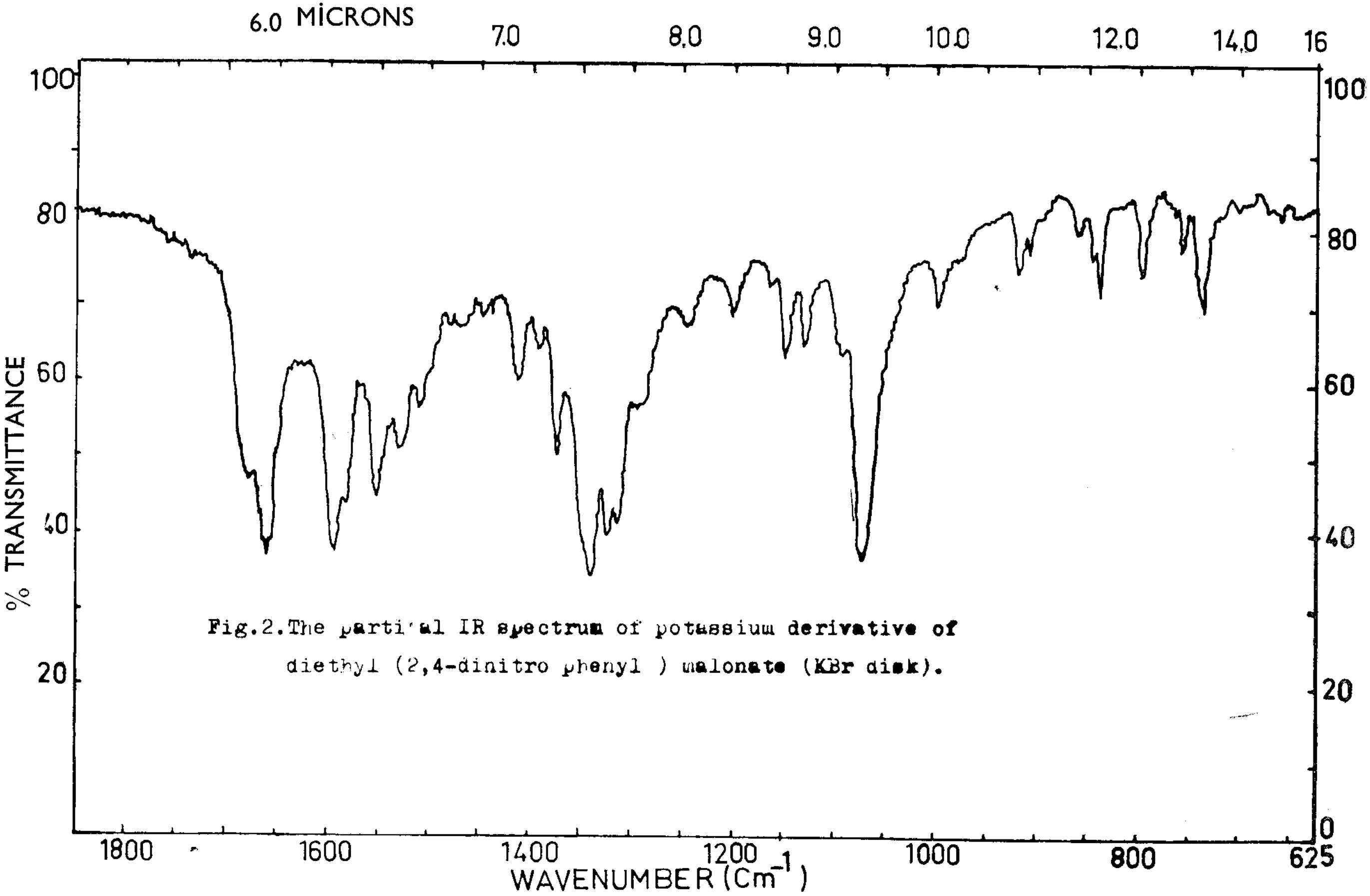

Fig.2.The partial IR spectrum of potassium derivative of diethyl (2,4-dinitro phenyl) malonate (KBr disk).

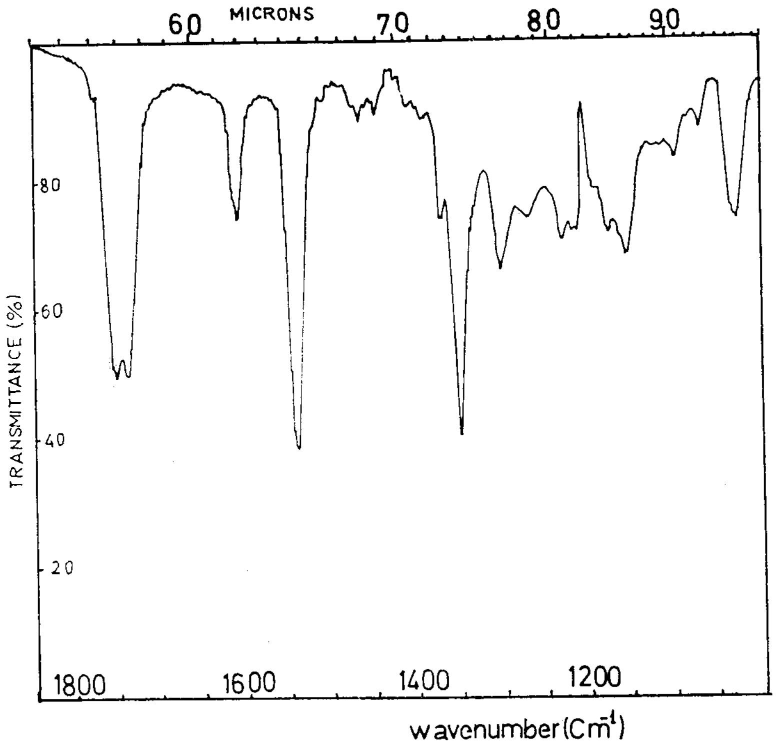

Fig. 3. The partial IR spectrum of diethyl (2,4-dinitro phenyl) malonate (KBr disk)

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