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Isolation and Structure Proof of Dinitrocyclohexenones Formed in the Nitration of Polyalkylbenzenes with Fuming Nitric Acid[1]

Hitomi SUZUKI,* Mikio SAWAKI,** and Reiji SAKIMOTO**
*Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto
**Research Institute, Nihon Soda Co., Ltd., Kohdzu, Odawara

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Action of fuming nitric acid upon 1,2,3,5-tetramethylbenzene and 2-ethyl-1,3,5-trimethylbenzene at low temperature was found to yield small amounts of dinitrocyclohexenones in addition to the ring nitration and side-chain nitrooxylation products. Chromatographic separation over silica gel followed by spectral investigation established the structures of these nitro-ketones to be 2,3,4,6-tetramethyl-5,6-dinitro-3-cyclohexen-1-one and 2,4,6-trimethyl-3-ethyl-5,6-dinitro-3-cyclohexen-1-one respectively. The mechanistic interpretation of their formation was briefly discussed.

Treatment of polyalkylbenzenes with fuming nitric acid at low temperature often yields a mixture of ring nitration and side-chain nitrooxylation products.[2] This unusual reaction has an electrophilic feature and is characterized for its peculiar orientation and high positional selectivity.[3] When the samples of the product mixtures from the nitration of polyalkylbenzenes were directly subjected to infrared analyses, it was usually noted that in addition to the major bands due to aromatic nitro compounds and benzyl nitrates, some weak absorptions occur in the regions attributable to carbonyl and aliphatic nitro group stretching vibrations. Carbonyl absorption would at first sight appear to arise from benzaldehydes which could be derived from benzyl nitrates under the influence of acid catalyst,[4] while absorptions owing to aliphatic nitro group would be attributed to phenylnitromethanes, the presence of which was confirmed in some nitration products.[5] However, some of these bands often appear in the regions of too higher frequencies (1370—1380 and 1560—1570 cm^{-1} for nitro group, and 1740—1750 cm^{-1} for carbonyl group) to make such spectral assignment unanimously acceptable. PMR spectra of the crude nitration products from polymethylbenzenes also exhibited weak peaks at quite high field 8.5—9.0 τ, indicating the presence of protons of highly alkane character. These puzzling features of infrared and PMR spectra are now explained by the isolation of alicyclic nitro-ketones, 2,3,4,6-tetraalkyl-5,6-dinitro-3-cyclohexen-1-ones, from the nitration products of isodurene (1,2,3,5-tetramethylbenzene) and ethylmesitylene (2-ethyl-1,3,5-trimethylbenzene), respectively. The structural proof of these unusual products will be the major subject of the present report.

In the preceding paper,[6] we have reported that the chromatographic treatment on silica gel of the nitration product from ethylmesitylene gave from benzene eluates some nitro-carbonyl compounds as a syrupy substance, from which a new nitro-carbonyl compound was obtained as fine colorless needles melting at 140—141°C. The result of elemental analysis and the appearance of a very weak molecular ion at m/e 256 in the mass spectrum indicated that the compound had a molecular formula $C_{11}H_{16}N_2O_5$. Its infrared spectrum revealed the presence of two different nitro groups (1568, 1549, 1379, and 1340 cm^{-1}), a carbonyl group (1737 cm^{-1}), and a double bond (1688 cm^{-1}, weak). The double bond should not be conjugated with carbonyl group nor nitro group, since the ultraviolet spectrum in methanol showed only one weak and broad absorption band at 287—288 nm ($\varepsilon=265$). Nitro groups seem to be attached to the carbon atoms adjacent to the carbonyl group and the double bond, respectively, because the $n\rightarrow\pi^*$ transition at 287—288 nm was appreciably intensified and the carbonyl stretching vibration was substantially shifted to higher wave number. The presence of cyclic structure was confirmed by the examination of the mass spectrum, which exhibited prominent peaks at m/e 210 (M^+–NO_2), 180 (M^+–NO_2–C_2H_6), 164 (M^+–$2NO_2$), 149 (M^+–$2NO_2$–CH_3), 135 (M^+–$2NO_2$–CH_3–CH_2), 121 (M^+–$2NO_2$–CH_3–$2CH_2$), 107 ($C_7H_6OH^+$), 105 ($C_7H_6CH_3{}^+$), and 79 ($C_6H_7{}^+$). The structural detail was obtained from the PMR spectrum, which depicted the presence of one ethyl group (3H 9.12 t, 2H 8.42 q; $J=7$ Hz. A two-proton quartet was further coupled slightly to the lower-field one proton quartet at 3.91 τ), three methyl groups (3H 8.78 s; 3H 8.15 s; 3H 7.89 d, $J=1.7$ Hz), and two methine protons (1H 5.01 s; 1H 3.91 q, $J=1.6$ Hz. A one-proton quartet at 3.91 τ was coupled slightly to the methylene quartet at 8.42 τ). The PMR data offer the partial structures –C(Me)=C(Et)–CH(Me)–, –CH–, and –CMe–, which were compatible with the spectral evidences only when the product was formulated as 2,4,6-trimethyl-3-ethyl-5,6-dinitro-3-cyclohexen-1-one. The appearance of some methyl and methine protons at quite

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[5] H. Suzuki, *ibid.*, **43**, 879 (1970).

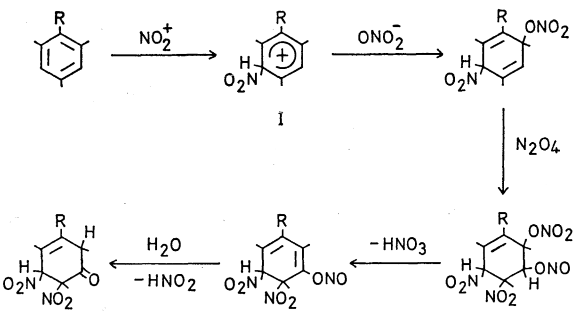
[6] H. Suzuki, M. Sawaki, and R. Sakimoto, *ibid.*, **45**, 1515 (1972).

high field in the PMR spectrum can be understood in terms of anisotropic effect of neighboring nitro groups.

Nitration of isodurene has been reported to yield mononitro or dinitro compounds.[7] However, the products were not as simple as had generally been thought, and besides normal ring nitration products, were obtained appreciable amounts of a non-crystallizable syrupy substance, which could be separated into two major fractions on silica gel chromatography; one containing side-chain nitrooxylated products and the other containing nitrocarbonyl compounds. Further treatment of the latter fraction on silica gel chromatography gave a nitro-ketone with the composition $C_{10}H_{14}N_2O_5$ as the main isolable product. It crystallized from ethanol as fine needles melting at 137—138°C. Its infrared spectrum contained absorption bands at 1738 (C=O), 1680 (C=C, weak), 1573 (NO_2), 1553 (NO_2), 1448, 1380 (NO_2), 1340 (NO_2), 1280, 1038, 1003, and 858 cm^{-1}, and its ultraviolet spectrum (in MeOH) showed a weak band at 285 nm (ε=327), which was characteristic of unconjugated ketones with $n \rightarrow \pi^*$ transition appreciably intensified by the presence of auxiliary chromophores. The PMR spectrum showed three methyl singlets at 8.72, 8.69, and 8.11 τ; one methyl doublet at 7.90 τ coupled to a lower-field methine quartet at 3.92 τ (J=1.5 Hz); and one methine singlet at 5.05 τ. These spectral data and the result of elemental analysis were only consistent with the formulation of the product as 2,3,4,6-tetramethyl-5,6-dinitro-3-cyclohexen-1-one. The assigned structure was further confirmed by the mass spectrum which showed the expected peaks at m/e 196 (M^+–NO_2), 166 (M^+–NO_2 –$2CH_3$), 150 (M^+–$2NO_2$), 135 (M^+–$2NO_2$–CH_3), 121 (M^+–$2NO_2$–CH_3–CH_2), 107 ($C_7H_6OH^+$), 105 (C_7H_6-CH_3^+), 91 ($C_7H_7^+$), and 79 ($C_6H_7^+$).

The formation of nitrocyclohexenones seems to be general in the nitration of highly alkylated benzenes, although these nitro-carbonyl compounds derived from various hydrocarbons are in most cases a non-crystallizable oil of complicated character, which gradually turned to a dark sticky substance on either repeated attempts to crystallize from solvents or prolonged standing.

The present result is of special interest, not only because it provides a novel mode of abnormal nitration but also because it seems to suggest the possibility of the addition-elimination sequence to be involved partly in the nitration of polyalkylbenzenes, which has generally been accepted to proceed through the S_E2 mechanism. The reaction sequence for the formation of 5,6-dinitro-3-cyclohexen-1-ones may be explained in terms of the addition-elimination mechanism which involves nitronium ion as electrophile and nitrate ion as nucleophile at the initial stage of the reaction. One of the plausible sequences is depicted in Scheme 1. The carbonium ionic intermediate (I) may be stabilized by the favorable orientation of alkyl substituents to such an extent that the addition process in which the nucleophile is captured can compete well with the ordinary substitution process. The process is supported by the recent observation[8] that the nitration of 1,2,3-trimethylbenzene and 4-bromo-*o*-xylene with acetic anhydride-nitric acid, a system containing a strong nucleophile, can lead to the extensive formation of 1-nitro-4-acetoxy-cyclohexa-2,5-dienes.



Scheme 1

Experimental

Infrared spectra were run as KBr disc on a Jasco DS-402G spectrophotometer and only prominent peaks are recorded. PMR measurements were carried out on a Varian A-60A and HA-100 spectrometer with deuteriochloroform as solvent and TMS as internal standard. Ultraviolet spectra were determined in methanol solutions on a Shimadzu QV-50 spectrophotometer. Mass spectra were obtained by Dr. A. Ohno of Sagami Chemical Research Center.

Isolation of Dinitrocyclohexenones. General procedures for the nitration of polyalkylbenzenes were described in the preceding paper. Although alumina chromatography was an efficient tool for the separation of side-chain substitution products from ordinary ring nitro compounds, it proved to be unsatisfactory for the isolation of dinitrocyclohexenones in crystallizable state from the crude nitration product mixtures. The oily nitration product was passed through a column of silica gel using light petroleum as eluant to give a mixture of nitro compounds and benzyl nitrates. Further elution with a mixture of benzene and light petroleum gave a fraction containing nitro-carbonyl compound as a yellow syrupy substance, which on trituration with ethanol gave a white powder in the crude yield of 2—4%. It was recrystallized several times from ethanol to give the nitro-ketone as colorless fine needles.

2,3,4,6-tetramethyl-5,6-dinitro-3-cyclohexen-1-one: mp 137—138°C.

Found: C, 49.75; H, 5.79%. Calcd for $C_{10}H_{14}N_2O_5$: C, 49.59; H, 5.79%.

2,4,6-trimethyl-3-ethyl-5,6-dinitro-3-cyclohexen-1-one: mp 140—141°C.

Found: C, 51.71; H, 6.40; N, 11.03%. Calcd for $C_{11}H_{16}N_2O_5$: C, 51.56; H, 6.25; N, 10.93%.

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