Electrogenerated Bases. VI. Reaction of Electrogenerated Superoxide with Some Carbon Acids. II.*

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Electrogenerated superoxide and molecular oxygen were allowed to react sequentially with a number of esters, nitriles, *N,N*-dialkylamides, sulfones, and aliphatic nitro compounds. The α -methyl groups in these compounds bore aliphatic and/or aromatic substituents. When the electron-withdrawing group (EWG) of these carbon acids could be displaced intact (nitrile 2, ArSO_2 4, nitro) good to excellent yields of the corresponding carbonyl compounds could be obtained. The efficiency of the transformation depended upon the nature of the substituents: α , α -diphenyl (*e.g.*, 2a) $>$ α -methyl- α -phenyl (2b) $>$ α , α -dimethyl. By conducting the electrolysis in the presence of acetic anhydride it was shown that the known conversion of phenylacetonitrile (2d) to benzoic acid did indeed proceed *via* benzaldehyde. When the EWG itself could be cleaved (esters 1, *N,N*-dialkyl-amides 3), this methodology produced α -hydroxylated compounds and the products resulting from fragmentation of the EWG and also from its complete displacement. The effects of the α -substituents were similar to those above.

Superoxide may function as a radical, an electron-transfer agent, a nucleophile, or a base. Examples of these behaviors are cited in Ref. 2. As part of a broader program in synthetic utilization of electrogenerated bases (EGB), we have here focused upon the behavior of carbon acids RH (electroinactive in these systems) of adequately low $\text{p}K_a$ toward a stream of O_2 which

is partially reduced to form the EGB $\text{O}_2^{\cdot-}$, *i.e.*, upon the sequential reactions $\text{RH} + \text{O}_2^{\cdot-} \rightarrow \text{R}^\cdot$, $\text{R}^\cdot + \text{O}_2 \rightarrow \text{products}$. (The deprotonation of the *O*-acid *n*-BuOH ($\text{p}K_a$ 33.3) is reported in Ref. 3.) For RH to be amenable to deprotonation by $\text{O}_2^{\cdot-}$ it must have within R one or more electron-withdrawing groups, so that a more appropriate general structural formula encompassing the types of compounds whose behavior is reported here is given by 1:

X=H, alkyl, aryl, RO ArO, *etc.*

Y=Z or H, alkyl, aryl

Z=electron-withdrawing group

1a, X=H, Y=CH₃, Z=COOEt

1b, X=H, Y=C₆H₅, Z=COOEt

1c, X=Y=CH₃, Z=COOCH₃

1d, X=Y=C₆H₅, Z=COOCH₃

1e, X=H, Y=Me₂CH, Z=COOEt

1f, X=H, Y=EtOCOCH₂, Z=COOEt

1g, X=H, Y=EtOCH₂CH₂CH₂, Z=COOEt

It was anticipated² that the nature of the reaction sequence would depend upon the identity of Y, particularly whether it could be displaced intact (*e.g.*, $-\text{NO}_2$) or in part (*e.g.*, COOR) or not at all, upon the $\text{p}K_a$ of I, and upon steric and electronic effects inherent in X and Y. For a series of malonate esters (1, Y=Z=COOR)

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was converted to benzoic acid, presumably *via* PhCHO. Superoxide is capable of deprotonating CH₃CN but in the work done the (CH₂CN)⁻ was not exposed to oxygen but rather trapped by PhCHO.⁷ Anions of *sec*-nitriles were (a) prepared at -78 °C *via* lithium diisopropylamide (LDA); (b) the anions reacted with O₂ to yield (c) after quenching with aqueous acid or acetyl chloride, hydroperoxide derivatives which were (d) reduced by Sn(II) to cyanohydrins; the latter on treatment (e) with alkali provided the final product ketones in excellent yields.⁸ Aromatic nitriles⁴ are inert toward O₂⁻.

- 2a, X=Y=Ph
 2b, X=Ph, Y=Me
 2c, X=Y=Me
 2d, X=H, Y=Ph
 2e, X=H, Y=Me
 2f, X=Y=H

Electroreduction of O₂ in the presence of selected nitriles 2 under our "standard" conditions (see Experimental) provides a convenient "one-pot" method for oxidative decyanation. The data are gathered in Table 2.

Good yields of ketones were obtained from *sec*-nitriles containing at least one aromatic substituent (2a, 2b). Isobutyronitrile (2c) gave only 20 % of acetone. Due to the anticipated instability in this system of aldehyde intermediates produced from primary nitriles,⁶ electrolyses in these cases were carried out both in the absence and in the presence of acetic anhydride. Primary nitriles (2d, 2e) were converted to carboxylic acid in the absence of Ac₂O and to the aldehyde diacetates in its presence. Acetonitrile (2f) behaved similarly. In all cases conversions were poor when only aliphatic substituents or H were at the α-position; the inadequately low pK_a of these derivatives toward reaction with O₂⁻ is of greater importance than the small steric effects of the Ph groups in 2a–2b, and 2d.

In the case of the nitriles 2 and of the classes of compounds discussed below it was of interest to attempt to determine the fate of the leaving group (Z in 1). For this purpose the products of

Table 2. Reaction of O₂⁻+O₂ with selected nitriles.^a

Nitrile (No.)	F mol	Products	Yields (%)
Ph ₂ CHCN (2a)	0.8	Ph ₂ CO MeNCO and trimer ^b	95 75
PhCH(CH ₃)CN (2b)	1.0	PhCOCH ₃ 2b	72 20
Me ₂ CHCN (2c)	1.0	(CH ₃) ₂ CO 2c	20 74
PhCH ₂ CN (2d)	1.8 1.8 ^c	PhCOOH PhCOOH PhCH(OAc) ₂	89 27 54
CH ₃ CH ₂ CN (2e)	1.0 1.0	CH ₃ COOH CH ₃ COOH CH ₃ CH(OAc) ₂	15 ^d 5 ^d 18 ^d
CH ₃ CN (2f)	0.22 0.22 ^c	HCOOH HCOOH CH ₂ (OAc) ₂	0.18 ^{e,f} 0.04 ^{e,f} 0.14 ^{e,f}

^a H-cell, Hg cathode, Pt anode. DMF/Bu₄NBr. O₂ stream, -1.0 V vs. SCE. 4–5 mmol of substrate. ^b After addition of MeI to the catholyte. See text. ^c Ac₂O present. ^d 75–80 % of 2e recovered. ^e mol/F. ^f 70–73 % of 2f was recovered.

olefins, albeit sometimes very slowly.¹⁰ The presumed hydroperoxide anion intermediates formed by the action of $O_2^- + O_2$ on the compounds discussed in our paper participate in several competitive followup reactions: transfer of oxygen to the parent carbanion,² nucleophilic displacement of a leaving group, reduction to alcohol; their effectiveness as epoxidizing agents will require that means be found for suppressing all other available routes. Up to the present, very small yields (<5 %) of epoxides have been obtained from styrene and stilbene, respectively, by including these olefins in electrolytic experiments with **3a**. Styrene alone with O_2^- is reported¹¹ to yield no oxygenated products.

Sulfones. Only two representatives of **4** were studied in order to augment the generality of the behaviour of **1** when Z is an intact leaving group.

4a, X=Y=Ph

4b, X=Me, Y=Ph

4a, after passage of 2 F/mol, yielded 90 % of benzophenone; **4b** (1.5 F/mol) gave 25 % of acetophenone. Addition of MeI to the catholyte after electrolysis in the presence of **4a** produced 65 % of methyl benzenesulfonate; the latter is also formed from sulfinate (as $\text{Bu}_4\text{N}^+\text{SO}_2\text{Ph}^-$) with O_2 alone or $O_2 + O_2^-$. These results contrast with those reported above for **2a**.

Nitro compounds. The very facile conversion by this methodology of a variety of *sec*-aliphatic nitro compounds, including those containing other functionalities such as keto-, ester, aryl to their corresponding ketones has been reported separately.¹ Additional examples, incorporating new features, have now become available. *Primary nitro compounds* (I, X or Y=H, Z=NO₂), as do other active methylene compounds with α -methylene rather than α -methinyl, reacted poorly. 1-Nitrononane after short electrolysis (0.62 F/mol) yielded 36 % nonanal. Starting material (16 %) was recovered but no carboxylic acid was found. Longer electrolysis (1 F/mol) yielded an unresolved mixture of products not containing acid. An attempt to intercept the intermediate aldehyde by reducing O_2 in the presence of

1-nitropentane and Ac_2O was unsuccessful: 16 % of pentanoic acid and 33 % of starting material was obtained but no aldehyde diacetate. Nitrocycloolefins (e.g., **5**, **6**) were converted to the

respective α,β -unsaturated ketones in good yield. Nitro compounds under basic conditions are known²⁴ to form hydroxamic acids which decompose on hydrolysis to carboxylic acids.

EXPERIMENTAL

Study of esters.¹² A conventional H-cell with a G5 sintered glass diaphragm was used. The cathode was a 20 cm² Hg pool, the anode a Pt foil. The potentiostat was manufactured by Ultraschalltechnik Co. of Halle (DDR). The ¹H NMR spectra (in CDCl₃ with hexamethyldisilane or tetramethylsilane as internal standards) were obtained using an 80 MHz instrument BS 847C of Tesla; the mass spectra employed a Varian Match 6. For thin layer chromatography (0.2 mm) DC Alufolien Kieselgel 60 (Merck) was used; for preparative chromatography (PC) 2 mm. Developing agents were benzene (B), ethyl acetate (E) and methanol (M).

The *general electrolysis procedure* was as follows. About 1–3 g of starting ester, 100 ml of dry DMF together with 10 g of activated neutral Al₂O₃ dried at 400 °C at 5 Torr for at least 5 h¹³ and 0.01 mol of Et₄NBr were charged into the catholyte. The anolyte contained solvent/supporting electrolyte and 5 ml of cyclohexene. A stream of dry O₂ was bubbled through the catholyte. Electrolysis at –0.9 to –1.0 V vs. SCE was stopped after passage of 1 F/mol. Workup followed one or more of these procedures: (A) The DMF was removed from the catholyte *in vacuo*; the residue was extracted repeatedly with ether; the ether extract was washed with water, dried and evaporated to remove solvent. (B) like (A) except that the water washes were re-extracted with ether+CHCl₃, the extracts washed with a minimum of water, dried and combined with the above extracts. (C) The DMF was removed under N₂. The residue at 0 to –5 °C was brought to pH 10 and taken to dryness. The new residue was dissolved in the minimum amount of H₂O, adjusted to pH 1 with dilute HCl, and extracted several times with CHCl₃.

The extracts were washed minimally with water, dried and the solvent evaporated. (D) The catholyte at 0 to -5°C was added to 200 ml of 3.5 % HCl. Distillation under N_2 to 155°C yielded a distillate containing DMF, $\text{HCl}/\text{H}_2\text{O}$ and products. The distillate was brought to pH 10 with 1N NaOH and evaporated to dryness under N_2 . The residue was then treated as in (C).

Methyl isobutyrate (1c). 2.05 g of ester, after electrolysis, yielded 0.97 of crude product which after purification by PC using B:E:M in the ratio 1:2:1 yielded purified α -hydroxyisobutyric acid (R_F 0.35–0.45). After sublimation at 49°C the product had R_F 0.39. The IR spectrum showed OH at 3450 cm^{-1} and $>\text{C}=\text{O}$ at 1695 cm^{-1} . The MS (70 eV) showed m/e (%): 104(3), 73(100), 59(82). ^1H NMR (CDCl_3): δ 2.72 (S, 3H, CH_3), 2.82 (S, 3H, CH_3) and 7.94 (S, 1H, OH). The product was identical with an authentic sample.

Methyl diphenylacetate (1d). Electrolysis of 2.26 g at -0.95 V was followed by workup (A) to yield 1.25 g of crude. Purification by PC using B:E of 10:1 yielded 1d (R_F 0.23), methyl α -hydroxydiphenylacetate (R_F 0.5) and benzophenone (R_F 0.7). The purified hydroxy-ester (R_F 0.52), a viscous yellow oil, was 45 % of the crude mixture. In the IR it showed absorption at 1725 cm^{-1} ($>\text{C}=\text{O}$) and at 3450 cm^{-1} (OH). The ^1H NMR (δ) showed a singlet for 3H of OCH_3 , a singlet at 4.11 (OH, exchangeable with D_2O) and a multiplet for 10 aromatic H at 7.15–7.50. The MS (70 eV) gave m/e (%): 242(12), 184(23), 183(100), 165(7), 152(8), 106(20), 105(95), 78(12) and 77(16). The benzophenone, 10 % of the crude after further purification, had R_F 0.68 and IR spectrum identical to that in the literature.¹⁴ The MS (12 eV) showed m/e (%): 182(100), 105(81), 77(66).

Diethyl succinate (1f). Electrolysis at -0.9 V and workup (B) gave 0.8 g crude product purified by PC using B:E:M at 1:2:1. About 4 % of *dl*- and *meso*-diethyl tartrate was obtained with IR spectrum identical to that reported.¹⁵

Study of the other carbon acids. Equipment. An H-cell with medium porosity sintered glass separator was used. The cathode chamber was provided with ports for gas inlet (glass frit), luggin capillary leading to an SCE, and removal of samples. The cathode was Hg (*ca.* 7.1 cm^2) and the anode a Pt foil (6.25 cm^2). Each compartment held *ca.* 60 ml. The potentiostat was a Wenking 70 HV1/90 and the digital coulometer model 640 supplied by the Electroynthesis Co. Analytical gas chromatography employed the Hewlett Packard model 5830A equipped with the HP 18850 data system; the column used was 1/8 in. $\times$ 0.5 m. 6 % SE-30. ^1H NMR spectra were taken on a Varian T-60 spectrometer (Me_4Si as internal

standard); IR spectra on a Perkin-Elmer 283, and mass spectra on a VG ZAB-2F. For preparative column chromatography there were used (a) a gravity glow silica gel column (Merck, silica 60, 70–230 or 230–280 mesh), (b) a Chromatotron (Harrison Research, Model 7924) with a 2 mm thick silica gel rotor (Merck, silica 60, PF-254) and (c) an Aerograph A-90P preparative GLC unit equipped with a 6 mm $\times$ 1.5 m 5 % SE-30 column whose temperature was 150°C . For thin layer chromatographic analysis Aldrich phosphomolybdic acid and an UV handlamp were used.

Materials. Acetonitrile (Mallinckrodt, spectral grade) was purified only by passage through a column of Sigma neutral alumina before use; the same solvent from other sources was first distilled under N_2 from P_2O_5 before the alumina treatment. Dimethylformamide was vacuum distilled first from calcium hydride then from anhydrous CuSO_4 . It was stirred over freshly activated 3A molecular sieves and passed through a column of alumina directly before use. Tetrabutylammonium bromide (Southwestern Analytical Chemicals, electrometric grade) was used as received. Molecular oxygen (Linde, 99.3 %) was passed through a 2 $\times$ 30 cm tube containing Drierite and NaOH pellets and then through 10A Molecular Sieves (Sigma) before it was admitted into the cell. The nitriles 2 were purchased from Aldrich and purified by distillation or recrystallization as appropriate. Bu_4NCN in DMF was made by double decomposition of Bu_4NCl (Aldrich) and NaCN (Mallinckrodt) in this solvent and used directly after removing the NaCl by filtration. The *N,N*-dialkylamides 3 were prepared from the acid chlorides and diethylamine in ether¹⁶ and purified by distillation under reduced pressure. Each showed only one component by GLC. The sulfones 4a¹⁷ and 4b¹⁸ were prepared according to the literature. IR, ^1H NMR and MS data as well as melting points were in agreement with the structures indicated. Tetrabutylammonium benzenesulfonate was prepared by acidifying the sodium salt (Aldrich), extracting into ether, evaporating to dryness, neutralizing with 40 % Bu_4NOH (Aldrich) and again concentrating and drying *in vacuo*. 1-Nitropentane¹⁹ and 1-nitrononane²⁰ were prepared according to the literature as were 1-nitro-1-cyclohexene (5) and bicyclo[4.4.0]nitro- $\Delta^{2,3}$ -decene (6).²¹

General procedure. The oven-dried H-cell was charged under Ar with 60 ml of solvent and 0.2 M *n*- Bu_4NBr in each compartment. The solutions were pre-electrolyzed at -1.2 or -1.9 V vs. SCE until the background current decayed to 10 and 1 mA, respectively. Cyclohexene (*ca.* 1 ml) was added to the anolyte to trap liberated bromine and *ca.* 4 mmol of substrate was added to the

catholyte. Oxygen was bubbled through the catholyte; the cathode potential was controlled at -1.0 V. The consumption of the starting material was monitored by periodic TLC or GLC analysis. The workup procedure depended on the solvent that had been used: (a) when it was DMF the catholyte was poured into 60 ml of ice-water, the solution extracted with 5×100 ml of ether, the ether extracts washed with water, dried over MgSO_4 , filtered and taken to dryness; when it was CH_3CN , about 80 % of the solvent from the catholyte was removed using a rot-o-vap with water aspirator, ether was added, the combined solutions washed with water and brine, dried (MgSO_4), filtered, and concentrated *in vacuo*. Deviations from this general procedure, necessitated by the physical properties of the starting material or products, are noted below.

Diphenylacetoneitrile (2a). The general procedure (DMF) was followed. The ether residue after workup was benzophenone identical with an authentic sample. In other experiments designed to identify the composition of the leaving fragment, the electrolyzed catholyte (pH 10) was brought to pH 8–9 by addition of HOAc. Argon was bubbled through the solution to displace excess O_2 and MeI was added. After one hour's stirring GLC analysis (SE-30 column) showed the presence of a small quantity of methyl isocyanate. After addition of water to the catholyte, a white precipitate was formed which, after recovery by filtration and recrystallization from ether–methanol, was shown to be trimethyl isocyanurate, m.p. 176°C , unchanged by admixture with an authentic specimen.²²

2-Phenylpropionitrile (2b). Electrolysis under the general conditions (DMF) yielded 72 % of acetophenone and 20 % of unchanged starting material which were separated by column chromatography (ethyl ether–pentane). Each component was identical to a respective authentic sample.

Isobutyronitrile (2c). Since it was anticipated that the expected product, acetone, would be swept out of the cell by the O_2 stream, a trap containing aqueous 2,4-dinitrophenylhydrazine sulfate was attached to one of the ports of the cathodic chamber. After the electrolysis, the derivative was found in the trap and no acetone, as judged by the same test, remained in the catholyte. Aqueous workup of the latter yielded the amount of starting material indicated (Table 2).

Phenylacetoneitrile (2d). The starting material (3 mmol) was entirely consumed after 1.8 F/mol had been passed according to the general procedure (DMF). The workup procedure depended upon whether or not Ac_2O (3 mmol) had also

been added to the catholyte. In the absence of the anhydride the electrolyzed catholyte was brought to pH 3 by dilute HCl and extracted with several portions of ether. The ether extracts were washed, dried over MgSO_4 , filtered, and evaporated to dryness yielding authenticated PhCOOH. When Ac_2O had been included in the catholyte, the latter was diluted with cold water and directly extracted with ether. From the extract authenticated benzaldehyde diacetate was isolated.²³ The catholyte was then acidified to pH 3, extracted with ether, *etc.* to recover PhCOOH.

Propionitrile (2e) and acetoneitrile (2f). In each case, a Dry Ice–acetone cold finger was attached to the cathode chamber. The results given in Table 2 are typical of many experiments in which the system DMF/ $n\text{-Bu}_4\text{NBr}$ was used. The ratio of Ac_2O to substrate was varied from 0 to 10. Generally a current of 85–110 mA was passed until 2000–2500 coulombs had been used. Products and unchanged starting materials were determined by GLC.

Tetrabutylammonium cyanide. The DMF solution of this cyanide as prepared above was charged to the cathode compartment of the cell. Bu_4NBr was added and O_2 was bubbled through for 2 h. A sample was removed, treated with MeI and then examined by GLC. MeCN but no MeNCO or isocyanurate was detected. The remainder of the catholyte was electrolyzed similarly to 2a; after displacement of O_2 the catholyte was treated with MeI, *etc.*, yielding MeNCO and its cyclic trimer.

N,N-Diethyl diphenylacetamide (3a). Two traps, one with saturated $\text{Ba}(\text{OH})_2$ the other with 1 M HCl were attached to the cathode chamber. Standard electrolysis (DMF) with 4 mmol of 3a was carried out until the starting material had been consumed (1.5 F/mol). BaCO_3 and $\text{Et}_2\text{NH} \cdot \text{HCl}$ were recovered from the respective traps. Usual workup of the catholyte followed by column chromatography of the ether extracts on silica gel allowed separation of 2.2 mmol (54 %) of benzophenone and 1.6 mmol (40 %) of the α -hydroxylated N,N-diethylamide, m.p. 90°C , identical with a sample prepared according to the literature.⁹

N,N-Diethyl 2-phenylacetamide (3b). The procedure was similar to that used with 3a except that only 1.2 F/mol was arbitrarily used for the solution containing 4 mmol of 3b. The α -hydroxyamide, m.p. 84°C , was identical to the sample prepared according to Ref. 9.

N,N-Diethyl phenylacetamide (3d). Electrolysis was as in 3a, using 4 mmol of substrate and 1.8 F/mol. Workup of the acidified catholyte yielded the PhCOOH and the α -hydroxyamide,⁹ m.p. 43°C .

Diphenylmethyl phenylsulfone (4a). Standard electrolysis of a DMF solution containing 4 mmol of 4a was run until all the starting material had been consumed. The O₂ was displaced by Ar, MeI was added and the solution stirred for 1 h. Volatile materials were removed under reduced pressure. Addition of ether to the residue caused precipitation of n-Bu₄NBr which was removed by filtration. Column chromatography of the ether solution followed by elution with ether-pentane yielded 3.7 mmol (91 %) of benzophenone and 2.4 mmol (60 %) of methyl benzenesulfonate.

1-Phenylethyl phenyl sulfone (4b). 1 F/mol was used for the electrolysis of 1.6 mmol of 4b. The usual workup afforded 0.4 mmol (25 %) of acetophenone and unchanged starting material (0.91 mmol, 64 %).

Tetrabutylammonium benzenesulfinate dissolved in DMF+Bu₄NBr and treated with O₂ alone or O₂+O₂⁻ yielded after methylation methyl benzenesulfonate.

Nitro compound 5. The SSE was CH₃CN/n-Bu₄NBr. Electrolysis in the presence of 2.66 mmol of 5 at -1.1 V vs. SCE for 43 mins (1F/mol) yielded 73 % of cyclohexenone (7) as determined by GLC analysis on a 1.0 m 15 % SE-30 column using biphenyl as an internal standard and 46 % isolated yield (Kugelrohr distillation at 170 °C). ¹H NMR and IR spectra agreed with the expected. More by-products were obtained at a less negative cathode potential.

Nitro compound 6. The same SSE system as above was used. Electrolysis using 1.2 mmol of 6 at -1.0 V vs. SCE for 25 min (0.86 F/mol) yielded 59 % of the enone 8 and 20 % recovered 6. The compounds were separated by column chromatography using 15 % ether-Skelly Solve. The ¹H NMR and the IR spectra for 8 were satisfactory. Further, 8 was reduced completely with NaBH₄ in 1:1 ether-ethanol to the saturated alcohol identical by TLC, IR and GLC criteria with an authentic sample; the saturated alcohol on oxidation by the Jones Reagent yielded 2-decalone identical with a commercially available sample.

1-Nitrononane and 1-nitropentane. The same procedures as above were followed. The results have been presented in the Discussion.

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REFERENCES

1. Monte, W. T., Baizer, M. M. and Little, R. D. *J. Org. Chem.* **48** (1975) 803 (Part V).
2. Allen, P. M., Hess, U., Foote, C. S. and Baizer, M. M. *Synth. Commun.* **12** (1982) 123 and references therein.
3. Chin, D.-H., Chiericato, G., Jr., Nanni, E. J., Jr. and Sawyer, D. T. *J. Am. Chem. Soc.* **104** (1982) 1296.
4. Filippo, J. S., Jr., Romano, L. J., Chern, C.-I. and Valentine, J. S. *J. Org. Chem.* **41** (1976) 586.
5. Konen, D. A., Silbert, L. S. and Pfeffer, P. E. *J. Org. Chem.* **40** (1975) 3253.
6. Tezuka, M., Hanada, H., Ohkatsu, Y. and Osa, T. *Denki Kagaku* **44** (1976) 17.
7. Gibian, M. J., Sawyer, D. T., Ungermann, T., Tangpoonphalvivat, R. and Morrison, M. M. *J. Am. Chem. Soc.* **101** (1979) 640.
8. Selikson, S. J. and Watt, D. S. *J. Org. Chem.* **40** (1975) 267.
9. Wasserman, H. H. and Lipshutz, B. H. *Tetrahedron Lett.* (1975) 1731.
10. Rebek, J., Jr., McReady, R. and Wolak, R. *J. Chem. Soc. Chem. Commun.* (1980) 705; Rebek, J., Jr. *Heterocycles* **15** (1981) 538.
11. Feroci, G. and Roffia, S. *J. Electroanal. Chem.* **81** (1977) 387.
12. Humboldt University, Berlin, DDR.
13. Jensen, B. S. and Parker, V. D. *J. Chem. Soc. Chem. Commun.* (1974) 374.
14. *DMS-Spectral Cards, Documentation of Molecular Spectroscopy*, Butterworth, London 1967 and Verlag Chem., Weinheim/Bergstr., No. 9098.
15. *DMS-Spectral Cards, Documentation of Molecular Spectroscopy*, Butterworth, London 1967 and Verlag Chem., Weinheim/Bergstr., No. 1733.
16. Delaby, R., Reynaud, P. and Lilly, F. *Bull. Soc. Chim. Fr.* (1961) 2067.
17. Shriner, R. L., Struck, R. C. and Jorison, W. J. *J. Am. Chem. Soc.* **52** (1930) 2060.
18. von Braun, J. and Weissbach, K. *Ber. Dtsch. Chem. Ges. B* **62** (1929) 2416.
19. Kornblum, N., Larson, H. O., Blackwood, R. K., Mooberry, D. D., Oliveto, E. P. and Graham, G. E. *J. Am. Chem. Soc.* **78** (1956) 1497.

20. Wollenberg, R. H. and Miller, S. J. *Tetrahedron Lett.* 35 (1978) 3219.
21. Corey, E. J. and Estreicher, H. *J. Am. Chem. Soc.* 100 (1978) 6294.
22. Fukui, K., Tamimoto, F. and Kitamo, H. *Bull. Chem. Soc. Jpn.* 38 (1965) 1568.
23. Knoevanagel, E. *Justus Liebigs Ann. Chem.* 402 (1914) 111.
24. Feuer, H. In Patai, S. Ed., *The Chemistry of Nitro and Nitroso Groups*, Interscience, New York 1969, Part 1, 463.

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